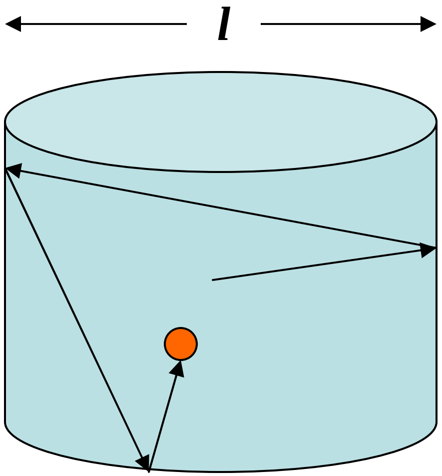
Vacuum Evaporation

Collision Rate

$K_n > 1$ Ballistic regime, minimal intermolecular interaction



l : A characteristic length of the chamber

$A \approx 4l^2$
$V \approx l^3$: Surface area and volume of the chamber

v : Average speed of a molecule

$\tau = l/v$: Time between each collision

$N_0 = 1/\tau = v/l$: Number of collisions a molecule will have in a second

$nl^3 N_0 = nl^2 v$: Total number of collisions of all the molecules will have in a second

$nl^2 v / A = nv/4$: Total number of collisions of all the molecules will have in a second per unit area

$$\boxed{\text{rate of collisions} = \frac{nv}{4} (\text{coll/s.cm}^2)}$$

Collision rate per unit area of molecules with a surface

… in more useful units

$$\text{rate of collisions} = \frac{nv}{4}\,(\text{coll/s.cm}^2)$$

Collision rate per unit area of molecules with a surface

$$n = P/k_B T$$

From the ideal gas equation

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$$

Average velocity of molecules

$$\frac{nv}{4} = \frac{1}{\sqrt{2\pi k_B}}\frac{P}{\sqrt{Tm}}$$

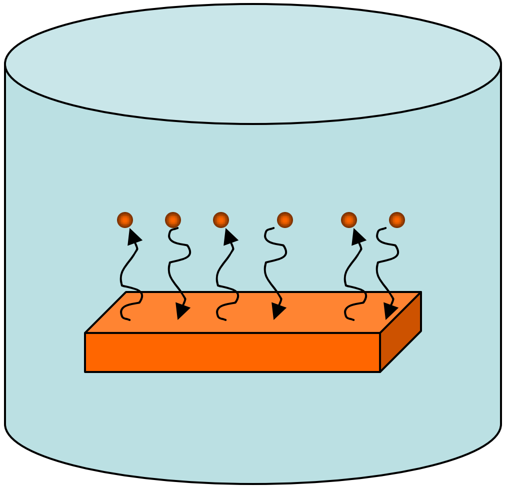
The collision rate in terms of P (in Pascals), T (in Kelvins) and the weight of a single molecule (m, in kg)

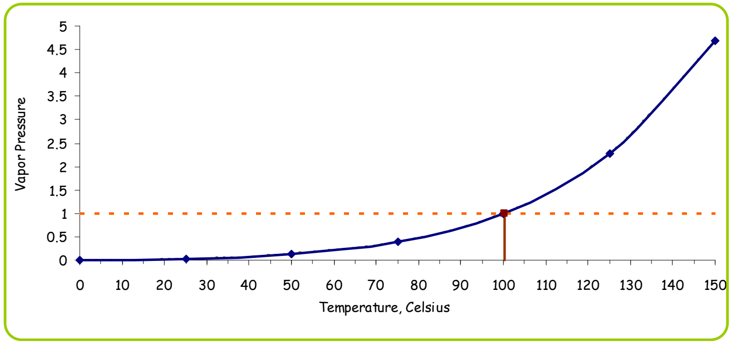
$$\boxed{\frac{nv}{4} = 3.51\times 10^{22}\,\frac{P}{\sqrt{TM}}}$$

The collision rate in terms of P (in Torrs), T (in Kelvins) and the molecular weight of the molecule (M)

Vapor Pressure

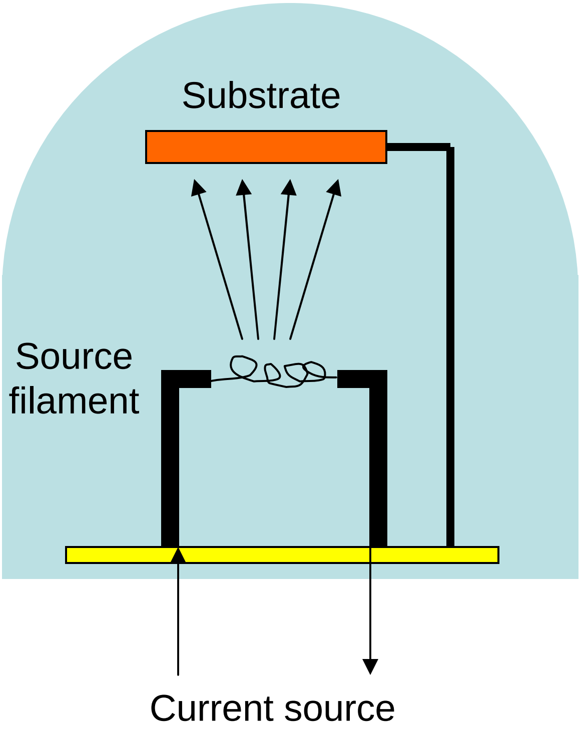
- This is the pressure of a vapor in equilibrium with its other phases (liquid and solid) at a given temperature.
- Place a material in a vacuum chamber and pump it down.
- Start from low T, so that P ~ 0
- Slowly increase T until you can detect P.
- This means that sublimation (evaporation) has started.
- The pressure will increase to an equilibrium value (**vapor pressure**).
- This is the point at which evaporation from the material is balanced by condensation.
- By changing the temperature of the material, vapor pressure can be changed.
- The relationship between P_V and T is determined by the Clausius-Clapeyron equation but generally experimental data is used.





Vacuum Evaporation

- 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 distance between the source and the substrate and the time of evaporation.



Things We Control

- When trying to figure out the correct parameters (P, T) to use in vacuum evaporation, we need to consider the evaporation rate, vapor pressure and the deposition rate.
- At the vapor pressure the collision rate is equal to the evaporation rate.

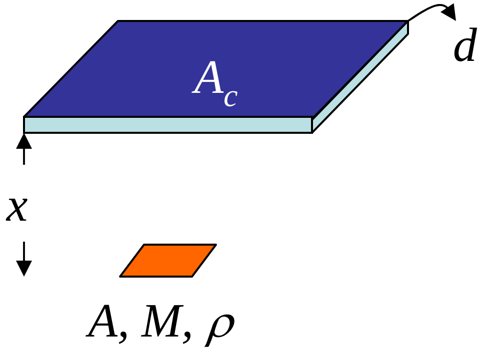
$$\boxed{\frac{nv}{4} = 3.51\times10^{22}\frac{P}{\sqrt{TM}}}$$

or in mass units

$$\boxed{\Gamma_e = 5.84\times10^{-2} P_V \sqrt{\frac{M}{T}}\,\frac{g}{cm^2 s}}$$

- The deposition rate is dependent on the geometry of the source, the substrate and the evaporation chamber.

A Very Rough Calculation of Deposition Parameters



$$V_c = A_c d$$ Volume of deposition

$$V_{molecule} = 1.66\times10^{-24}\frac{M}{\rho}$$ Volume of one molecule

$$N = \frac{V_c}{V_{molecule}} = \frac{A_c d}{1.66\times10^{-24}}\frac{\rho}{M}$$ Number of molecules to be deposited

$$\frac{N}{At} = \frac{A_c d}{1.66\times10^{-24}}\frac{\rho}{M}\frac{1}{At} = 3.51\times10^{22}\frac{P}{\sqrt{TM}}$$ Evaporation rate

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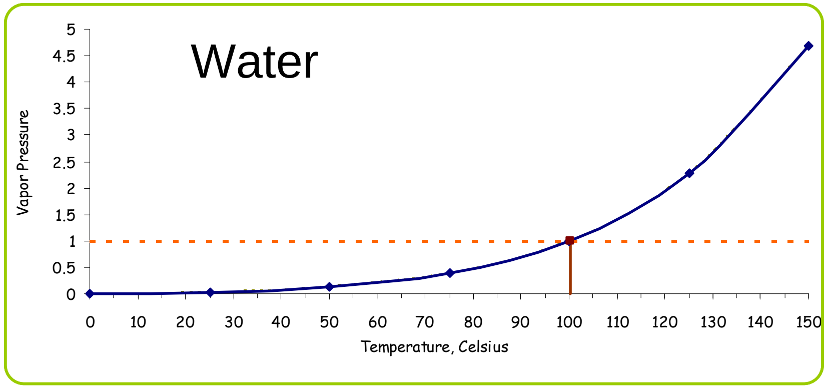
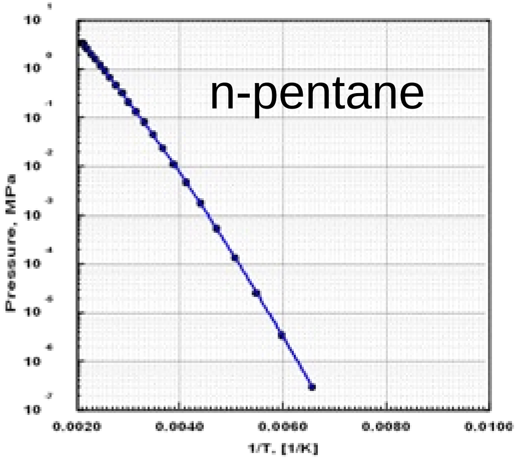
$$P = \frac{A_c d}{1.66\times10^{-24}}\frac{\rho}{M}\frac{1}{At}\frac{\sqrt{TM}}{3.51\times10^{22}} \longrightarrow \boxed{P = 17.2\frac{A_c d\rho}{At}\sqrt{\frac{T}{M}}}$$

The vapor pressure *P* at source temperature *T* that satisfies the deposition requirements.

Finding the Temperature

$$P = 17.2 \frac{A_c d\rho}{At} \sqrt{\frac{T}{M}}$$





- Use the vapor pressure curve for the source material to find the right P-T pair that satisfies the above equation (mostly by trial and error).
- The result is the required source temperature to achieve the desired deposition.

Deposition Example

$$A = 1cm^2$$

$$x = 10cm$$

$$d = 2500\,\overset{o}{\mathrm{A}} = 2.5\times10^{-5}cm$$

$$A_c = 100cm^2$$

$$t = 100s$$

$$\longrightarrow \quad P = 4.3\times10^{-4}\rho\sqrt{\frac{T}{M}}$$

For Magnesium, ρ = 1.74, M = 24.3

$$\longrightarrow \quad P = 1.52\times10^{-4}\sqrt{T}$$

1. Guess a pressure of 10^{-2} Torr
2. From the curve: T = 730 K
3. From the formula: P = 4.1 x 10^{-3} Torr
4. Guess P = 3.6 x 10^{-3} Torr
5. From the curve: T = 680 K
6. From the formula: P = 3.64 x 10^{-3} Torr
7. Good enough, heat Mg to 680 K

For Aluminum, ρ = 2.70, M = 27

$$\longrightarrow \quad P = 2.23\times10^{-4}\sqrt{T}$$

1. Guess a pressure of 10^{-2} Torr
2. From the curve: T = 1490 K
3. From the formula: P = 8.61 x 10^{-3} Torr
4. Guess P = 7.8 x 10^{-3} Torr
5. From the curve: T = 1460 K
6. From the formula: P = 7.84 x 10^{-3} Torr
7. Good enough, heat Al to 1460 K

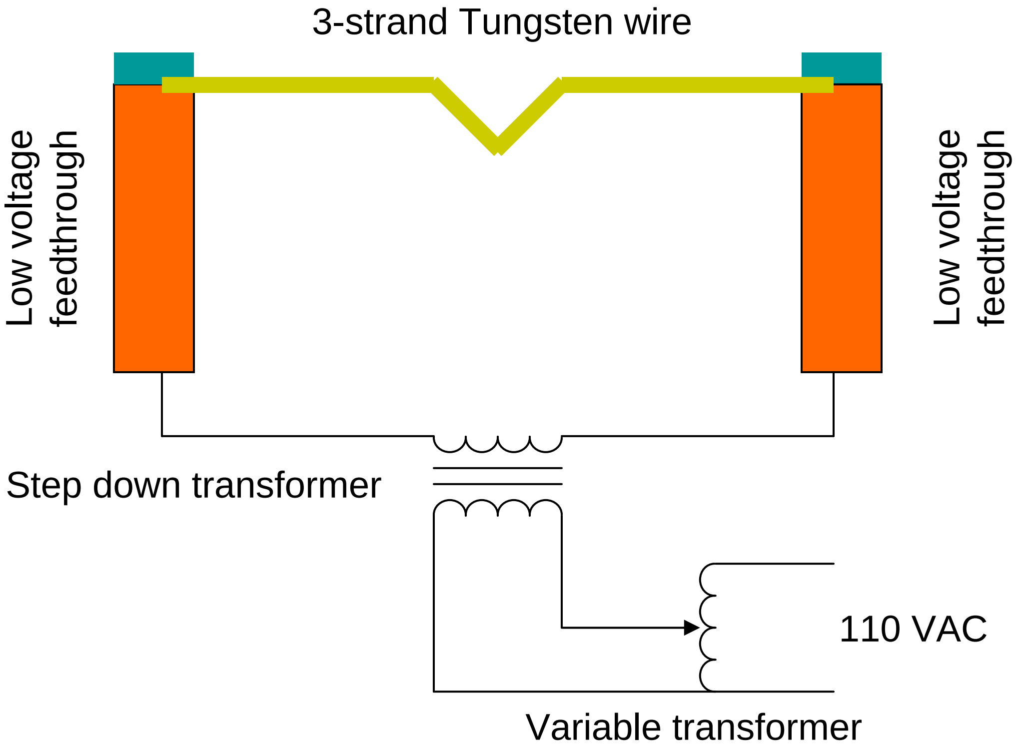
Some Things to Note …

- Small changes in temperature can dramatically change deposition rates (d/t).
  - For example, we found that to deposit Al at 25 A/s, we needed 1460 K. For a tenth of this rate (2.5 A/s) we would need 1340 K and for ten times this rate (250 A/s) we would need 1610 K.
- The evaporation rates are not affected by the degree of vacuum as long as the vacuum is high enough to be in the ballistic regime.
- You have to make sure that the source temperature for the desired deposition rate does not approach the melting point of the source. If it does, you may have to reduce the deposition rate.
  - For example, to achieve the previous deposition parameters for Ti requires a source temperature of 2000 K, which is coming close to the melting point of Ti at 3200 K. It may be necessary to lower the rate.

Vacuum Evaporation Sources

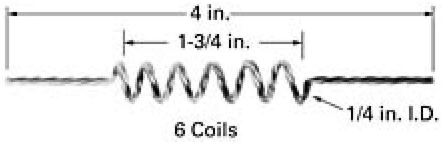
- Physical evaporation
  - A “source” container is heated.
  - The material to be evaporated is placed in or near the source.
  - The radiative and conductive heating evaporates the source.
- Electron beam evaporation
  - A filament is heated and emits electrons.
  - The electrons heat the evaporant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

The Basic V-Groove Source

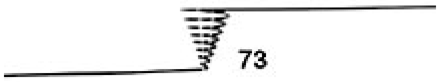


- Place the evaporant at the tip of the V.
- Uses radiative and conductive heating (through wetting) to evaporate material.
- Filament is good for one use.
- Not for depositing films thicker than 1500 A.
- Point source (fairly even coating over a spherical surface)

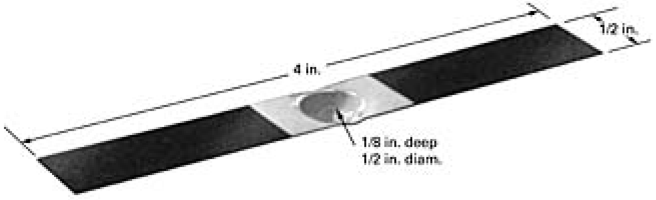
Other Arrangements



- **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.

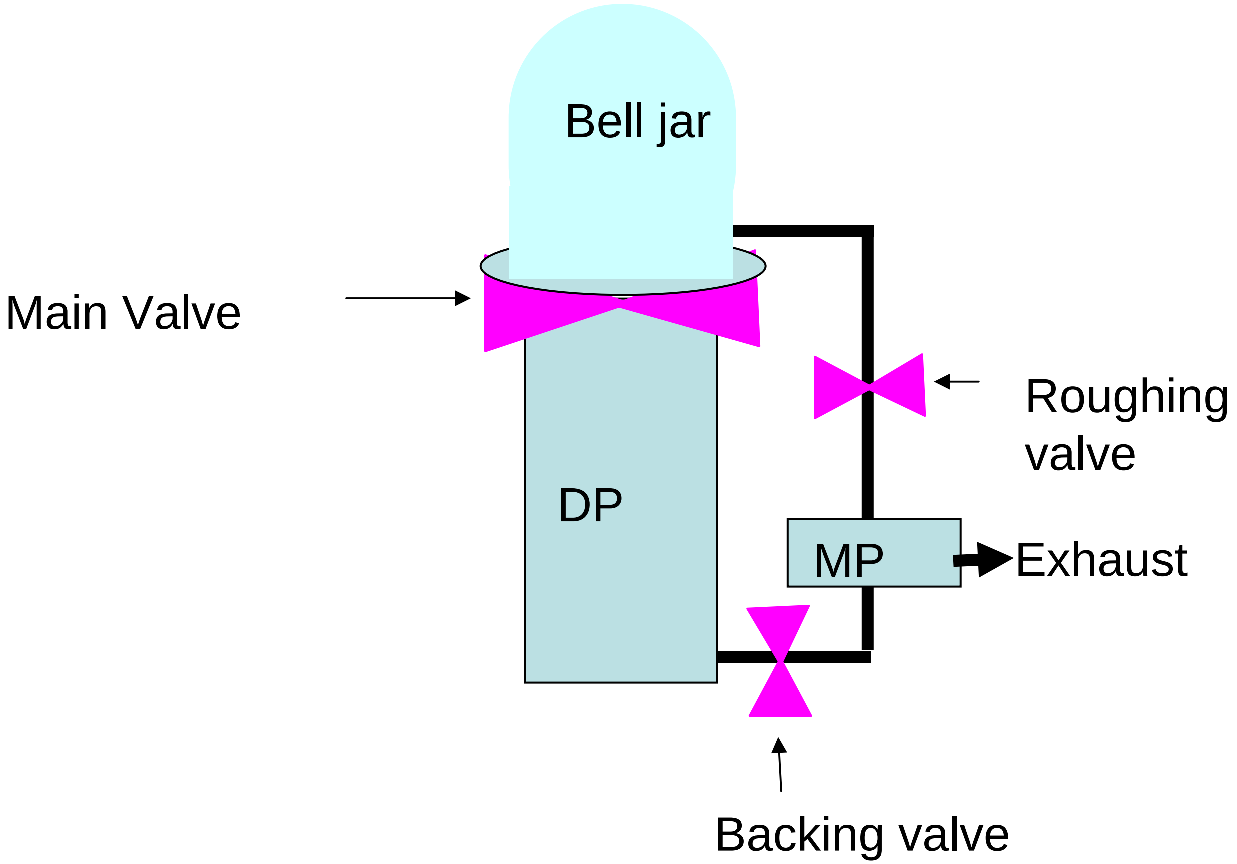
Quartz Crystal Monitors

- 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

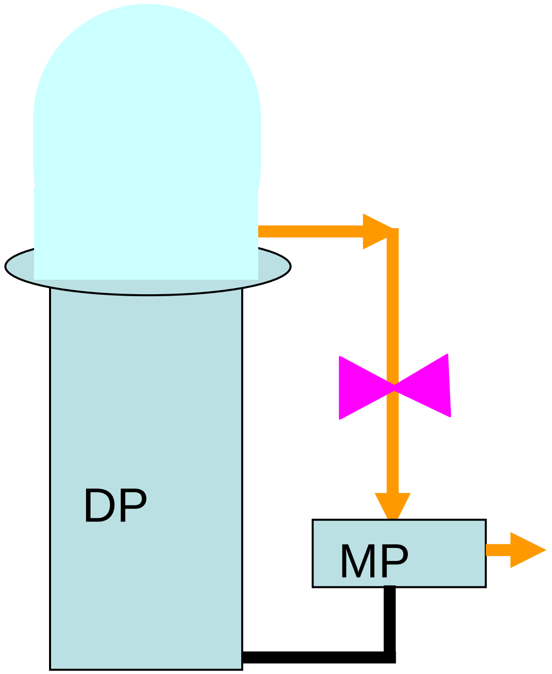


Complete vacuum evaporator

Operating situation 1: Making low vacuum in chamber

Roughing valve open:

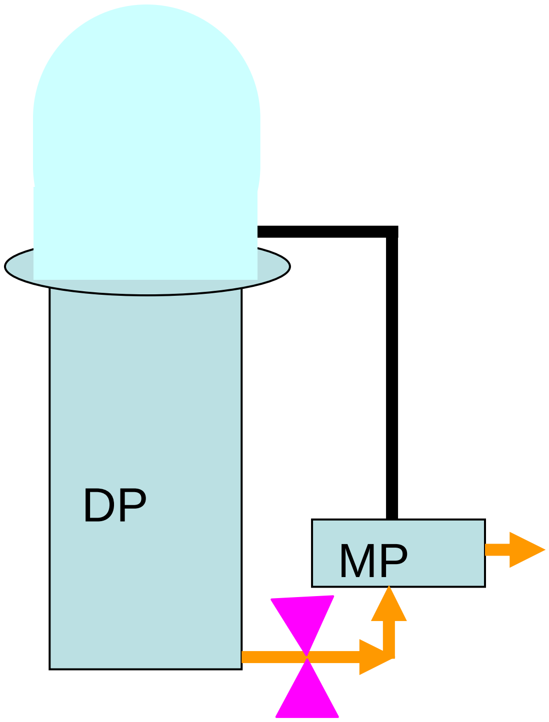
- MP makes low vacuum in chamber



Operating situation 2: Standby situation

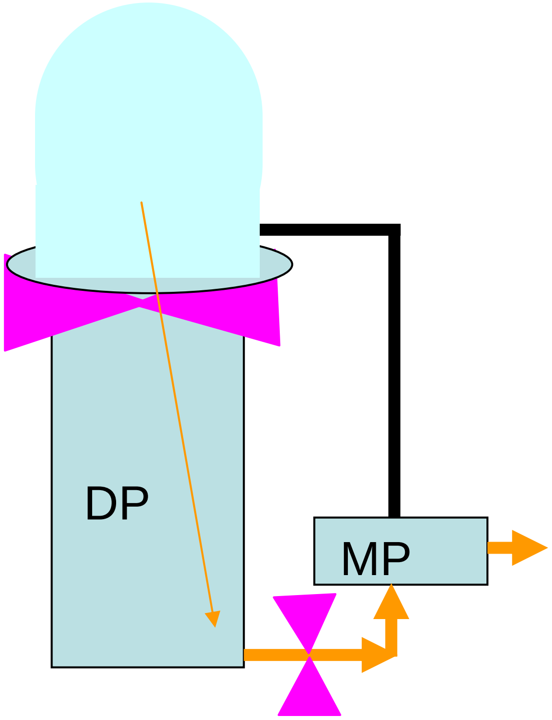
Backing valve open:

MP removes air molecules from DP



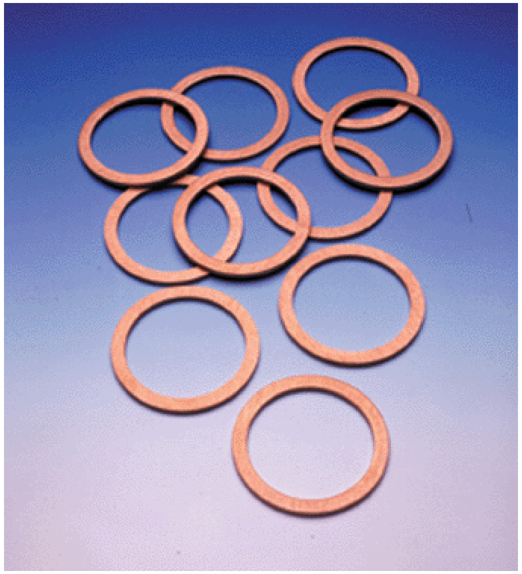
Operating situation 3: Condition for evaporation

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).