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Chair of Surface and Materials Technology

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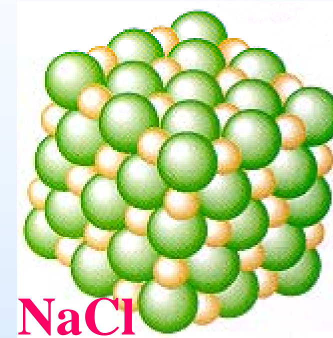
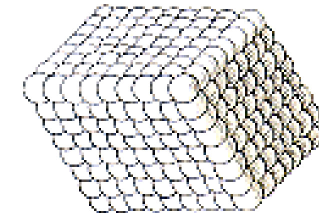
Fundamental Terms (1)

- **Solids**
- Very high levels of arrangement
- Limited mobility
- Coefficient of viscosity ~ 10^{11} Pa*s

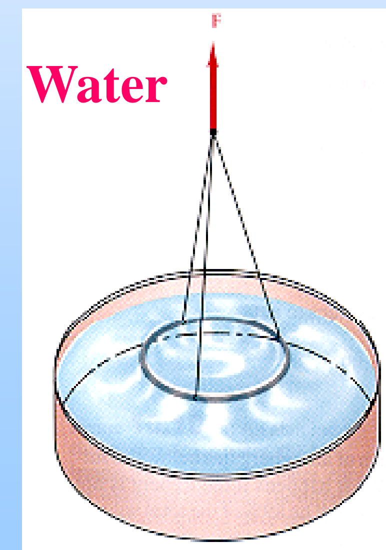


Calcite

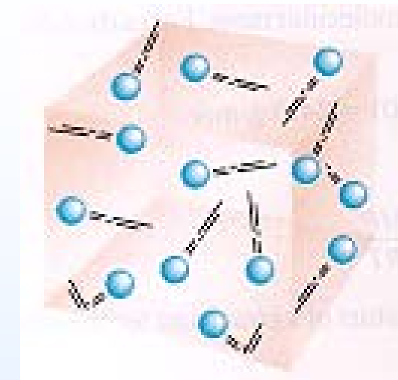


$\tau = \eta * D$
τ: Shear stress
D: Shear speed
η: Viscosity

- **Liquids**
- Closed arrangements
- Crystalline arrangements in small complexes (nm range)
- Easiness mobility



Fundamental Terms (2)



- **Gases**
- The simplest systems
- Atoms or molecules behaving as free entities
- Matters in the gas phase at the normal conditions
- Viscosity of air at standard conditions of low vacuum is 16 orders of magnitude lower (1.82×10^{-5} Pa*s)
- Gas behavior not simple when investigated in large ranges of temperatures and pressures.
- Deviation in gas properties – **real gas**
- When the deviations caused by the gas kind are negligible – **ideal gas**

- **Vapors**
- Matters passing to the gas phase by increasing temperature or pressure drop.
- Critical temperature
- Physical model of the ideal gas in the kinetic theory of gases

Kinetics of gases

$$f(\upsilon) = \frac{1}{n}\frac{dn}{d\upsilon} = \frac{4}{\sqrt{\pi}}\left|\frac{M}{2RT}\right|^{\frac{3}{2}} \upsilon^2 \exp - \frac{M\upsilon^2}{2RT}$$

$$\upsilon_m = \sqrt{\frac{2RT}{M}}$$

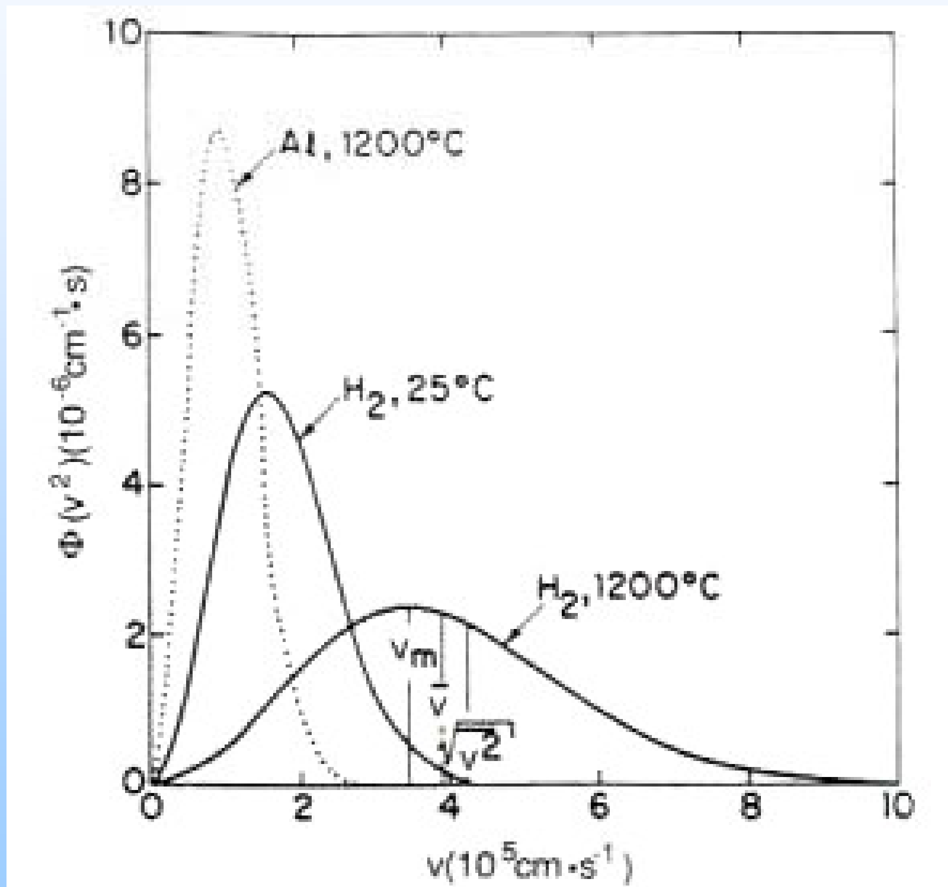
Maxwell-Boltzmann Equation,
M: Molecular weight
T: Absolute temperature
R: Gas constant

$$\bar{\upsilon} = \frac{\int_0^\infty \upsilon f(\upsilon)d\upsilon}{\int_0^\infty f(\upsilon)d\upsilon} = \frac{8RT}{\pi M}$$

Bei RT, 4,6 X 10^4 cm/s =1656 km/h

$$\overline{\upsilon^2} = \frac{\int_0^\infty \upsilon^2 f(\upsilon)d\upsilon}{\int_0^\infty f(\upsilon)d\upsilon} = \sqrt{\frac{3RT}{M}} \Rightarrow \left(\overline{\upsilon^2}\right)^{\frac{1}{2}} = \sqrt{\frac{3RT}{M}}$$

Velocity distribution of the gas molecules



Gas Pressure & Mean Free Path

$$P = \frac{1}{3}\frac{nM}{N_A}\overline{\upsilon^2} = \frac{nRT}{N_A}$$

N_A is Avogadro constant

1 atm = 1,013 x 10^6 dynes/cm^2 = 1,013 x 10^5 N/m^2

1 Pascal = 1 N/m^2

1 torr = 1 mm Hg = 1,333 x 10^3 dynes/cm^2 = 133,3 N/m^2 = 133,3 Pascal (Pa)

1 bar = 0,987 atm = 750 torr

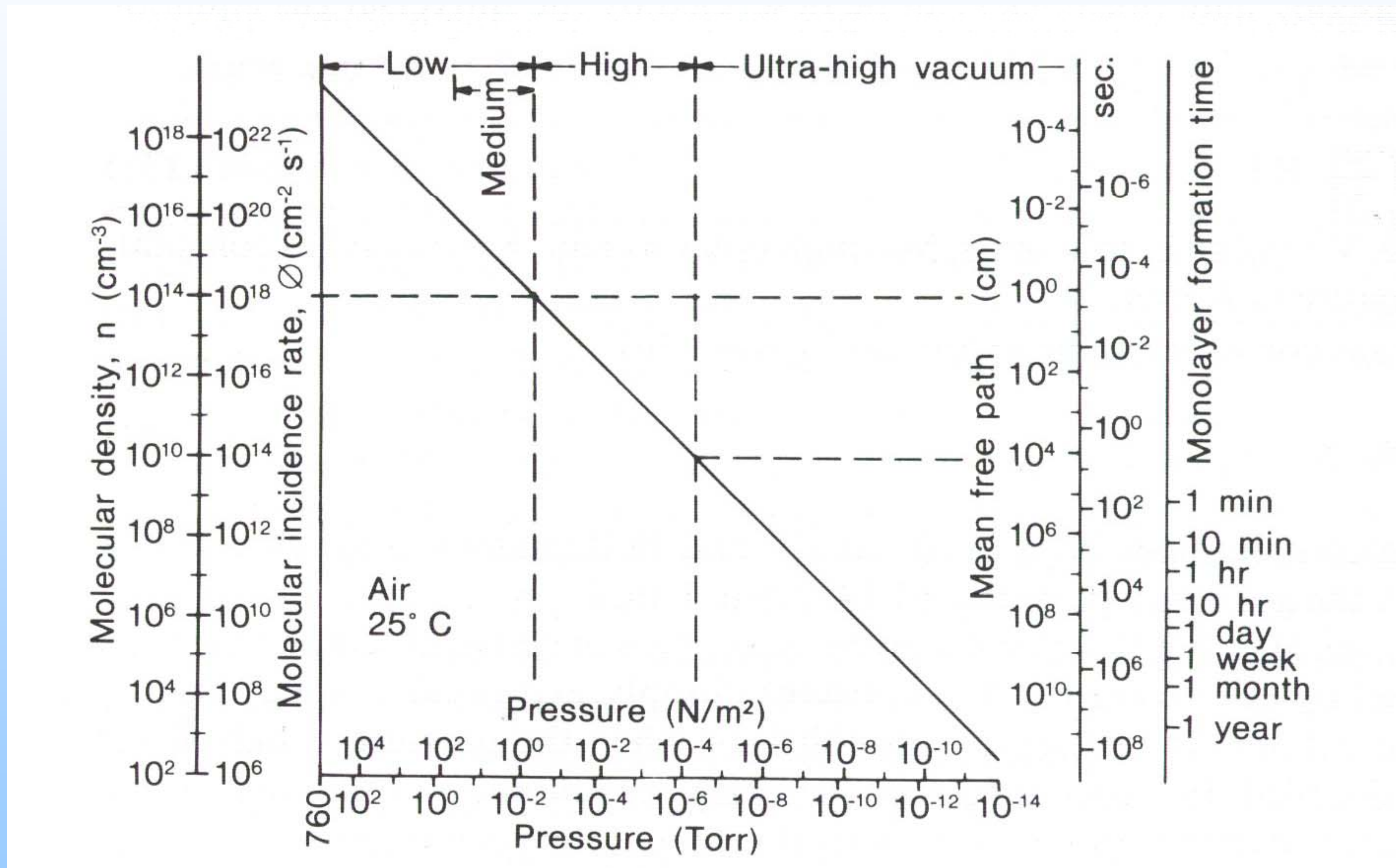
„Mean free path“

$$\lambda_{mfp} = \frac{1}{\pi d_c^2 n} = \frac{5\times 10^{-3}}{P}$$

If cm and torr are applied

d_c – Collision diameter of the molecules

Molecular density, incidence rate, mean-free path, and monolayer formation time as a function of pressure



Transport and Pumping of the Gases

$$C = 3.64A\left(\frac{T}{M}\right)^{1/2} = 11.7A$$

$$C = 19.4\frac{A^2}{BL}\left(\frac{T}{M}\right)^{1/2} = 12.2\frac{D^3}{L}$$

$$C = 3.81\frac{D^3}{L}\left(\frac{T}{M}\right)^{1/2} = 12.2\frac{(D_2 - D_1)^2(D_2 + D_1)}{L}$$

$$C = 9.70\frac{b^2c^2}{(b+c)L}\left(\frac{T}{M}\right)^{1/2} = 31.1\frac{b^2c^2}{(b+c)L}$$

$$C = 2.85D^2\left(\frac{T}{M}\right)^{1/2}\left(\frac{1}{1 + 3L/4D}\right) = 9.14\frac{D^2}{1 + 3L/4D}$$

$$C = 3.64\left(\frac{T}{M}\right)^{1/2}\left(\frac{A}{1 - (A/A_1)}\right) = \frac{11.7A_0}{1 - A_0/A_1}$$

$$C = 3.81\frac{D^3}{L}\left(\frac{T}{M}\right)^{1/2}\left(\frac{1}{1 + \frac{4D}{3L}\left(1 - \frac{D^2}{D_1^2}\right)}\right) = \frac{12.2D^3}{L\left[1 + \frac{4D}{3L}\left(1 - \frac{D^2}{D_1^2}\right)\right]}$$

Gas flow *Q* through *A*

$Q = C(P_1 - P_2)$

(torr-L/sec)

C = conductance,
Geometry dependent

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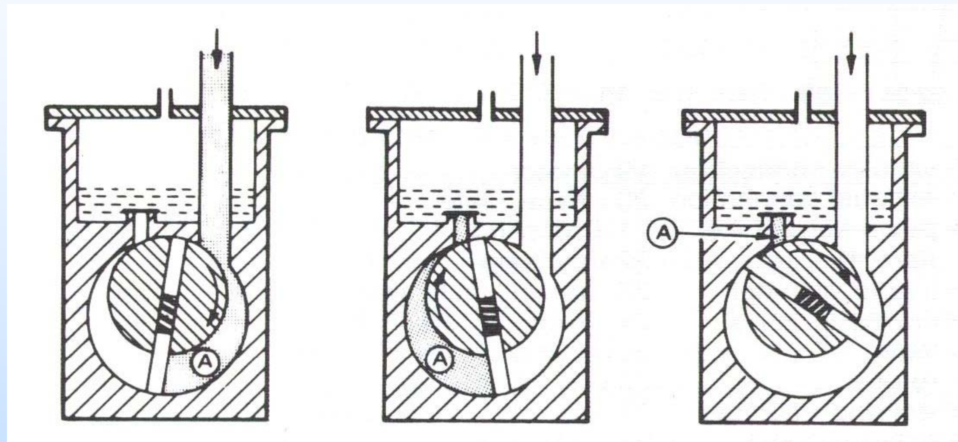
Pumping Systems (1)

- Mechanical displacement pumps – Rotary vane pump and Roots pump



Speed of rotation: 350 – 1400 rpm
Up to 2 * 10^{-3} mbar

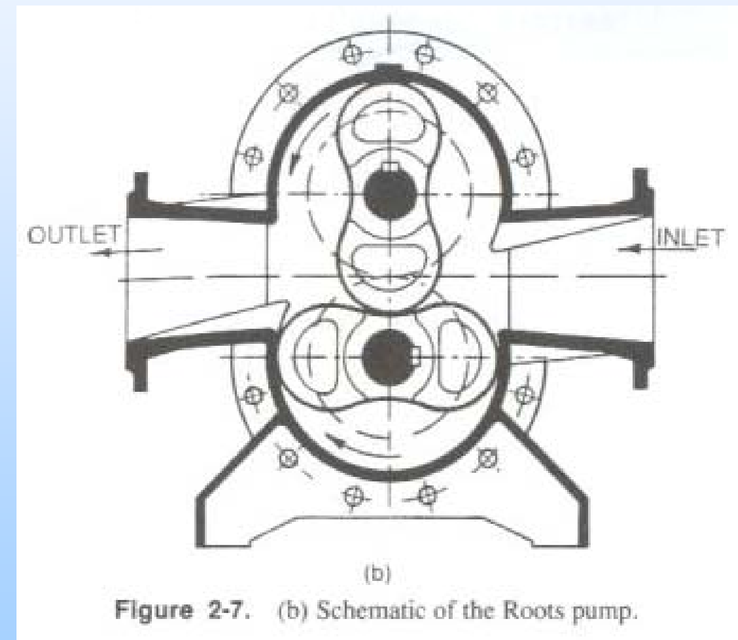


Figure 2-7. (b) Schematic of the Roots pump.

Higher speed of rotation due to absence of rubbing contact:
1000 – 3000 rpm

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Pumping Systems (2)

- Diffusion pump

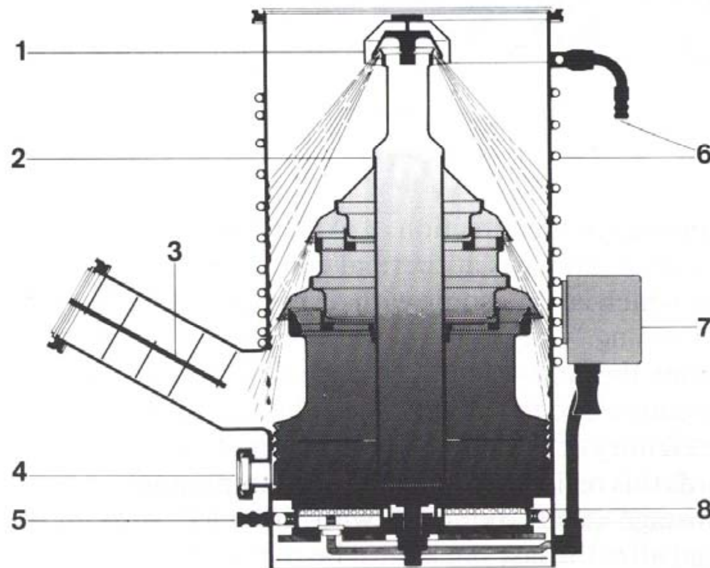

Fig. 26 a

Schematic representation of the operating principle of a diffusion pump.
1 = cold cap
2 = jet system with fractionating high vacuum stage
3 = fore vacuum baffle
4 = pumping fluid sight glass
5 = compressed air rapid cooling
6 = water cooling
7 = connection for thermal protection switch
8 = heater

Fig. 26 b
BALZERS oil diffusion pumps.

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Pumping Systems (3)

- Turbo-molecular pump

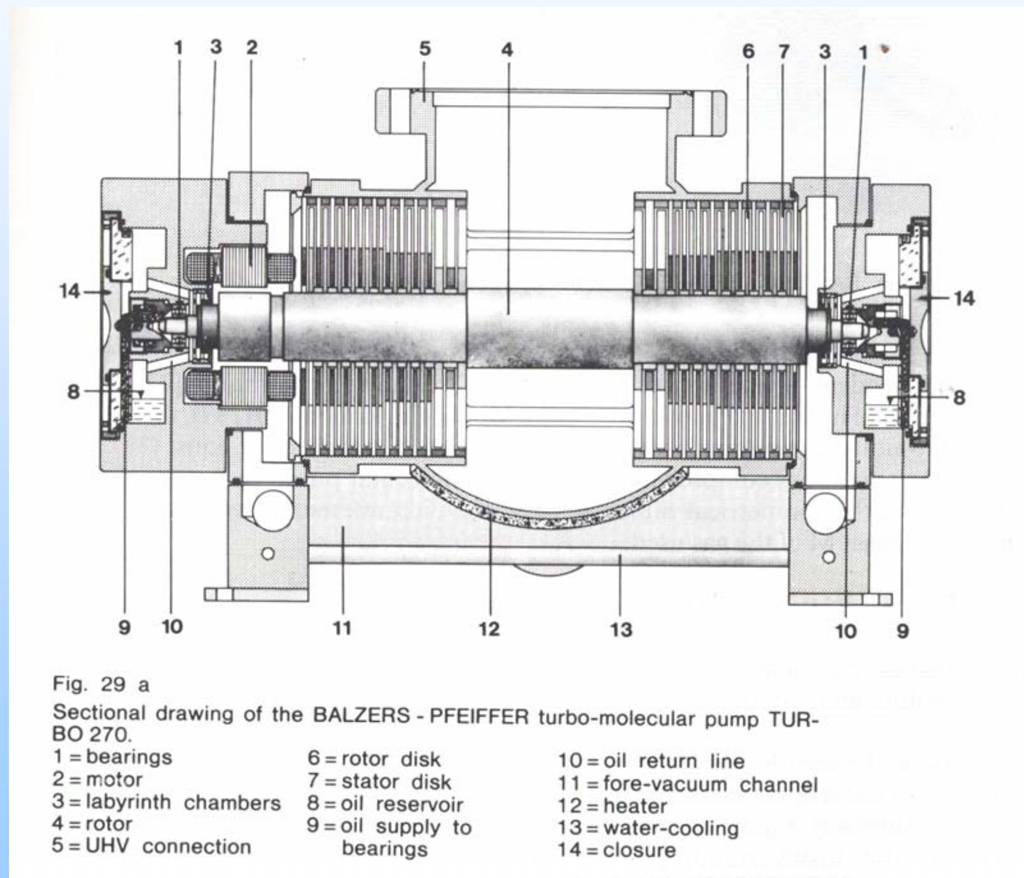
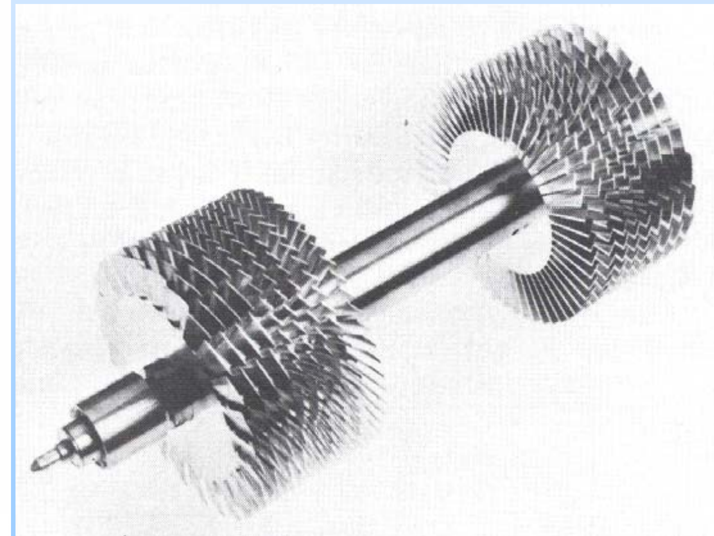


Fig. 29 a

Sectional drawing of the BALZERS - PFEIFFER turbo-molecular pump TURBO 270.

1 = bearings
2 = motor
3 = labyrinth chambers
4 = rotor
5 = UHV connection
6 = rotor disk
7 = stator disk
8 = oil reservoir
9 = oil supply to bearings
10 = oil return line
11 = fore-vacuum channel
12 = heater
13 = water-cooling
14 = closure



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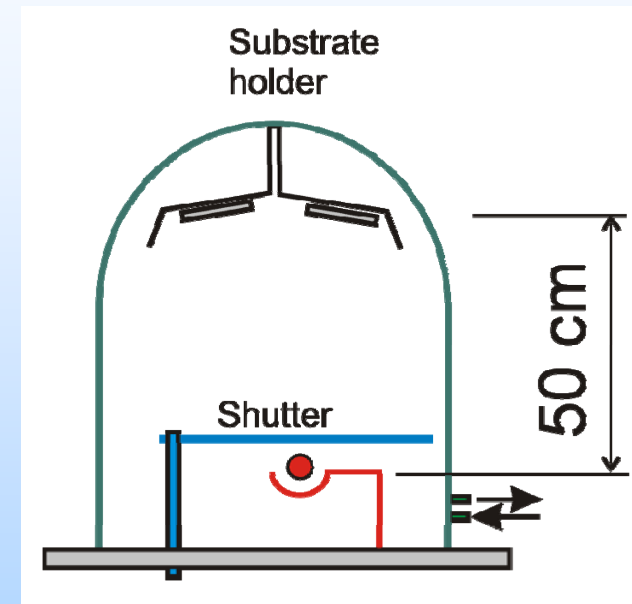
Thermal Evaporation

- Deposition - a mix of applied science and art with physics.
- Deposition in vacuum environment.



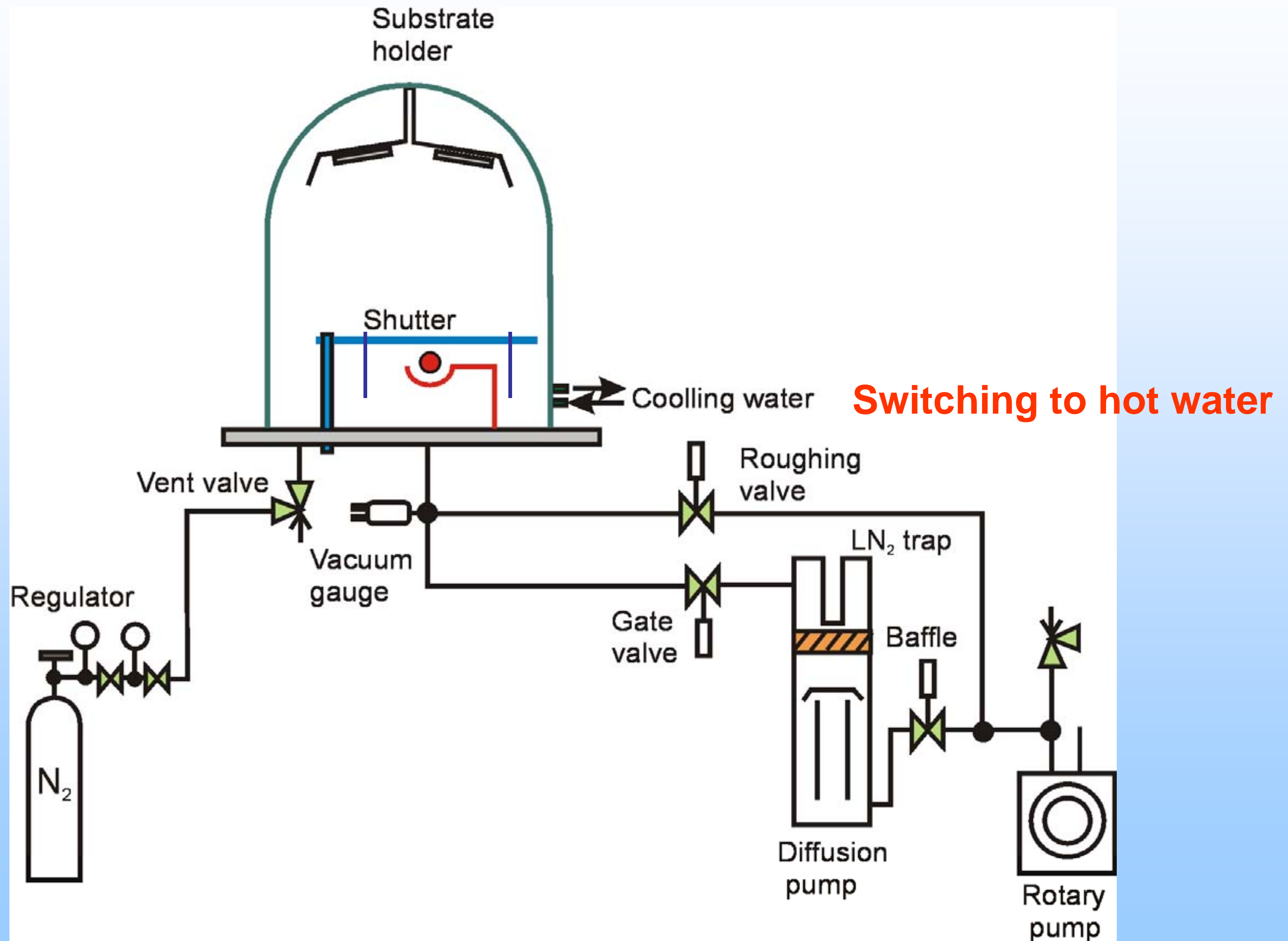
Vacuum Environment

- Vacuum is complex - not inert.
- Deposition with awareness of the effect of vacuum upon the vapor flux and growing film.

The three most important parameters relevant to vacuum

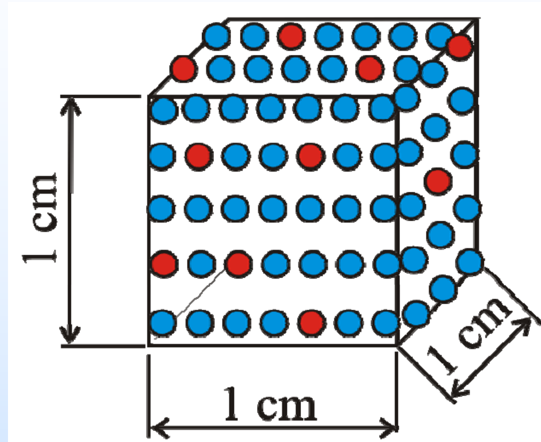
- Pressure - the mean free path (MFP).
- Partial pressure of reactive gases in inert working gases.
- Film vapor arrival to reactive gas impingement rate ratio.

Evaporation System



Switching to hot water

Mean Free Path - Scattering



Pressure [Torr]	Density [cm^{-3}]	Mean Free Path [m]	Scattered %
760	2.68×10^{19}	6.5×10^{-8}	100
10^{-5}	3.5×10^{11}	5	10
10^{-6}	3.5×10^{10}	50	1.0

MFP should be at least ten times the source to substrate distance.

Scaling up systems

- Increasing the source to substrate distance - deposition rate falls with the square of the distance.
- Increasing the source to substrate distance from 40 to 63 cm requires doubling the evaporation rate to maintain the arrival rate ratio or halving the pressure.

Necessity of the vacuum for evaporation

Avoidance of reactions between air and the materials, which should be evaporated (high temperature), whereby the source material will is contaminated

- Avoidance of collisions between molecules of evaporated substances and molecules of air in the vapor space, whereby the molecules evaporated cannot reach the substrate
- Avoidance of film impurities

Area density of surface atoms $10^{14}/cm^2$. Coverage of the surface lasts approx. 1 second at 10^{-4} to 10^{-5} mbar and with 25 °C

Hertz-Knudsen equation:

n - Concentration

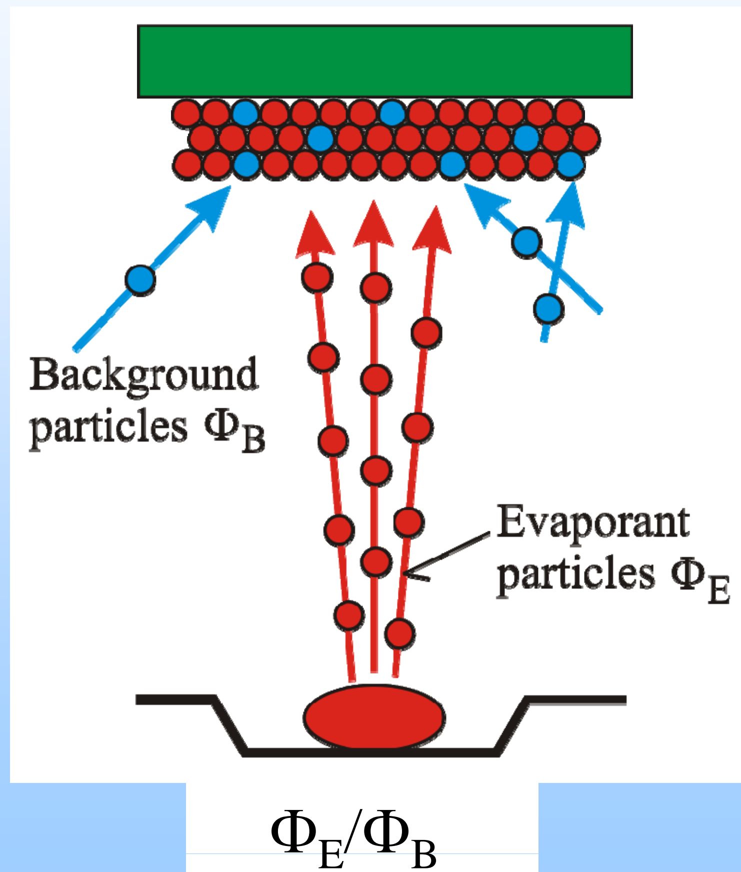
m - Mass

k – Boltzmann const.

v - Average velocity

$$J = \frac{dn}{dt} = n\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} = \frac{1}{4} n\bar{v}$$

Pressure - Arrival Rate Ratio



- In HV, residual gas –predominant water vapor.
- Maximum deposition pressure can be established for a thin film process upon its sensitivity to residual atm.
- Sputtering 99.9 % Ar at 10^{-3} Torr - residual contaminant 10^{-6} Torr.
- Reaction probability of contaminants in processing gas.
- Residual gas analyzer is required to determined contaminants.

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Effect of Vacuum Pressure on Films

The pressure may be taken as either the total pressure or the reactive gas partial pressure during deposition

Pressure [Torr]	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}
MFP [m]	5×10^{-4}	5×10^{-3}	0.05	0.5	5	50	500	5×10^{3}	5×10^{4}
Arrival Rate Ratio Φ_E/Φ_B	10^{-4}	10^{-3}	0.01	0.1	1	10	100	10^{3}	10^{4}

- Maintaining high film purity and arrival ratio of 10: It requires the total reactive gas pressure below 10^{-6} Torr.
- Film purity during growth of films by MBE, typically at 10^{-10} Torr.
- MBE requires low pressure because of the low (0.1 Å/s) deposition rate.

Vaporization Process

- Vapor flux of evaporant produced in a vapor source by energy supply.
- Transformation from solid/liquid to vapor phase occurs at certain pressure called saturated vapor pressure.
- Vapor flux condensed on a substrate.

- **Energy delivered to the evaporant source consists of**
  - Latent heat, the heat necessary to raise temperature of material to that where phase change occur.
  - Phase change heat, the heat of vaporization and the heat of fusion (for melting materials). This energy is the dominant energy required for vaporization.
  - Kinetic energy imparted to the vapor in excess of the minimum necessary for phase change.

Remarks

Latent heat and kinetic energy are negligibly small.

Major energy consumption is that need for vaporization.

For example, Al fusion heat is = 270 cal/cm^3, while vaporization heat is 78 kcal/cm^3

The evaporation temperature determines the kinetic energy of the evaporant

1000 °C $\approx$ 0.2 eV or 2000 °C $\approx$ 0.4 eV

This energy is the measure of the velocity of evaporant

In evaporation, the KE of the evaporant is limited to thermal energy.

The relationship between saturated vapor pressure and temperature can be find out using thermodynamic principles.

The Increase in KE of Evaporant and Implications

Ion plating and ion assisted deposition processes increase the energy of evaporant particles during the growth process

- By ionizing a working gas and accelerating it through 100-1000 V. -ion plating.
- Or bombarding the growing film from a low energy source using an energetic neutralized ion beam - ion assisted deposition.
- Both processes can increase the evaporant energy in one order of magnitude and even more.

- The added energy makes difference in
  - Film density
  - Film uniformity - coating holes and cracks,
  - Forming asperities, grain structure
  - Adhesion
  - Heating of substrates, etc.

Difference between evaporation and boiling

- **Evaporation & boiling** – transformation of other phase into vapors by heat supply.
- **Boiling** point: T at which the material changes from liquid to vapor at 1 atm.
- **Vacuum Vaporization: Evaporation** (in thin film deposition): Vapor pressure over evaporant surface is 0.1 – 1 Torr depending upon evaporation rate when the phase change occurs.

  Temperature is therefore much reduced from boiling point.

For example,

Al boils at 2300 ^{o}C and evaporates at 1080 ^{o}C at 1 Torr.

- From tabulated vapor pressure and equations the approximate evaporation temperature for many materials can be determined.

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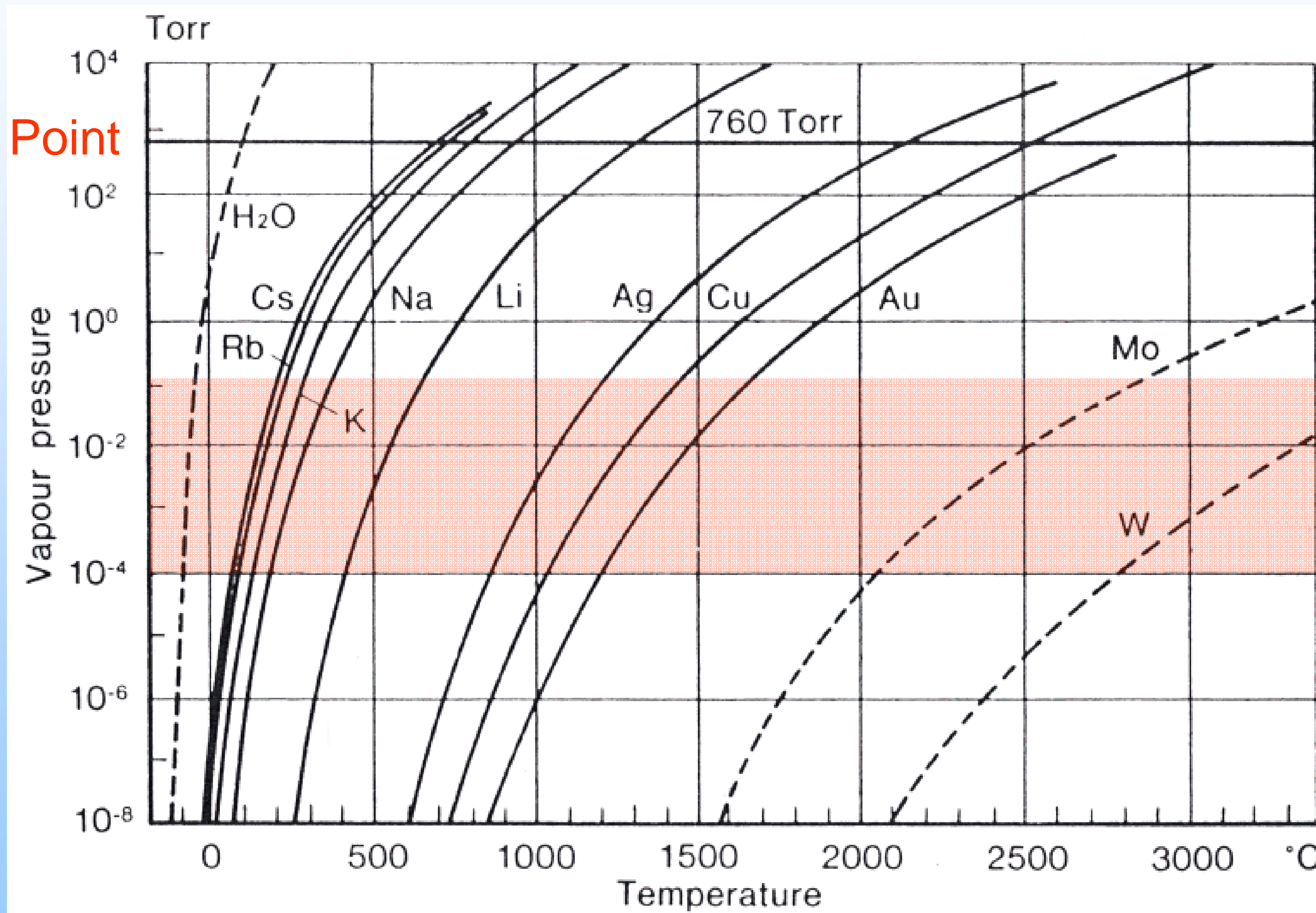
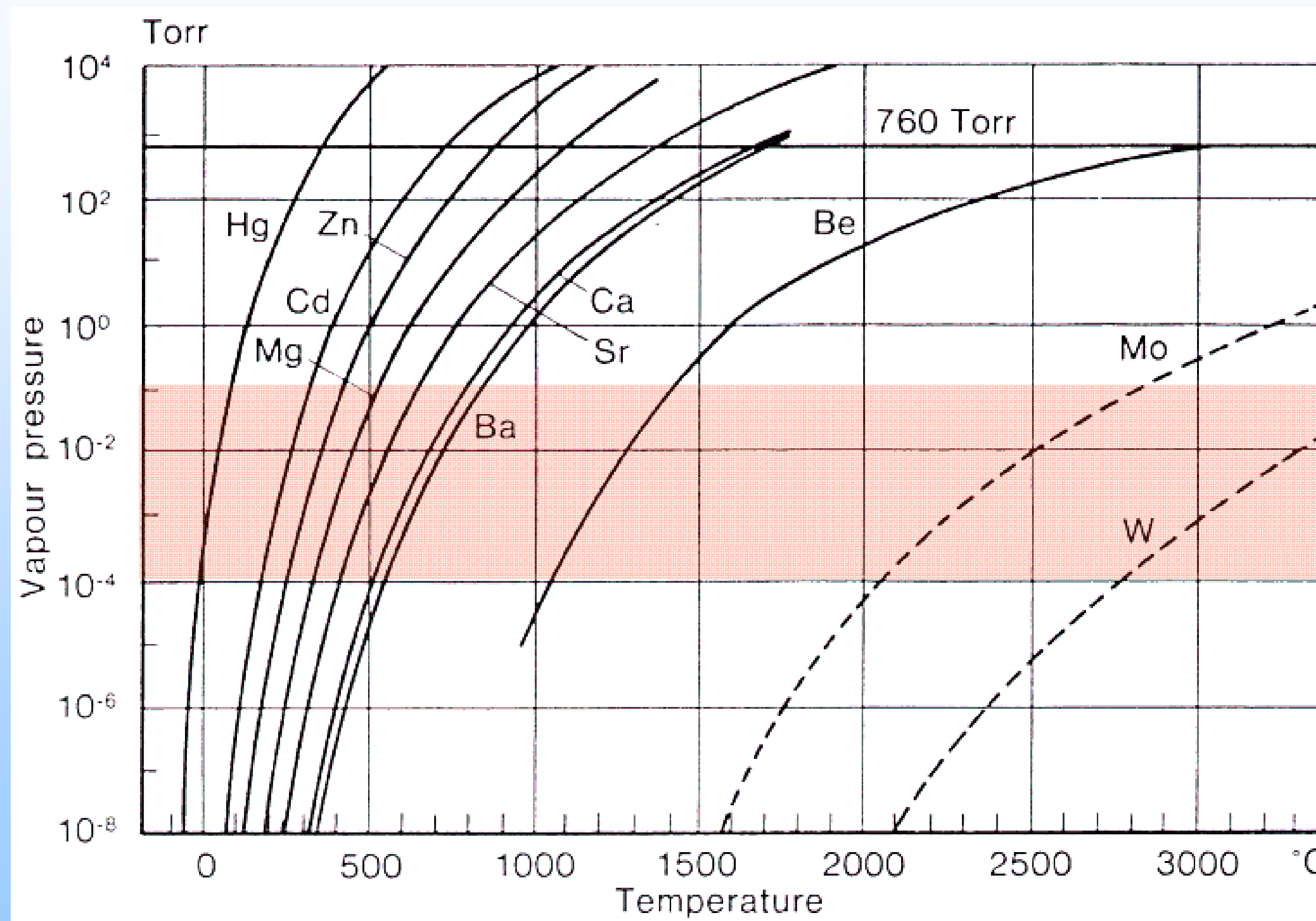
Saturated vapor pressure of 1. group elements dependent on temperature

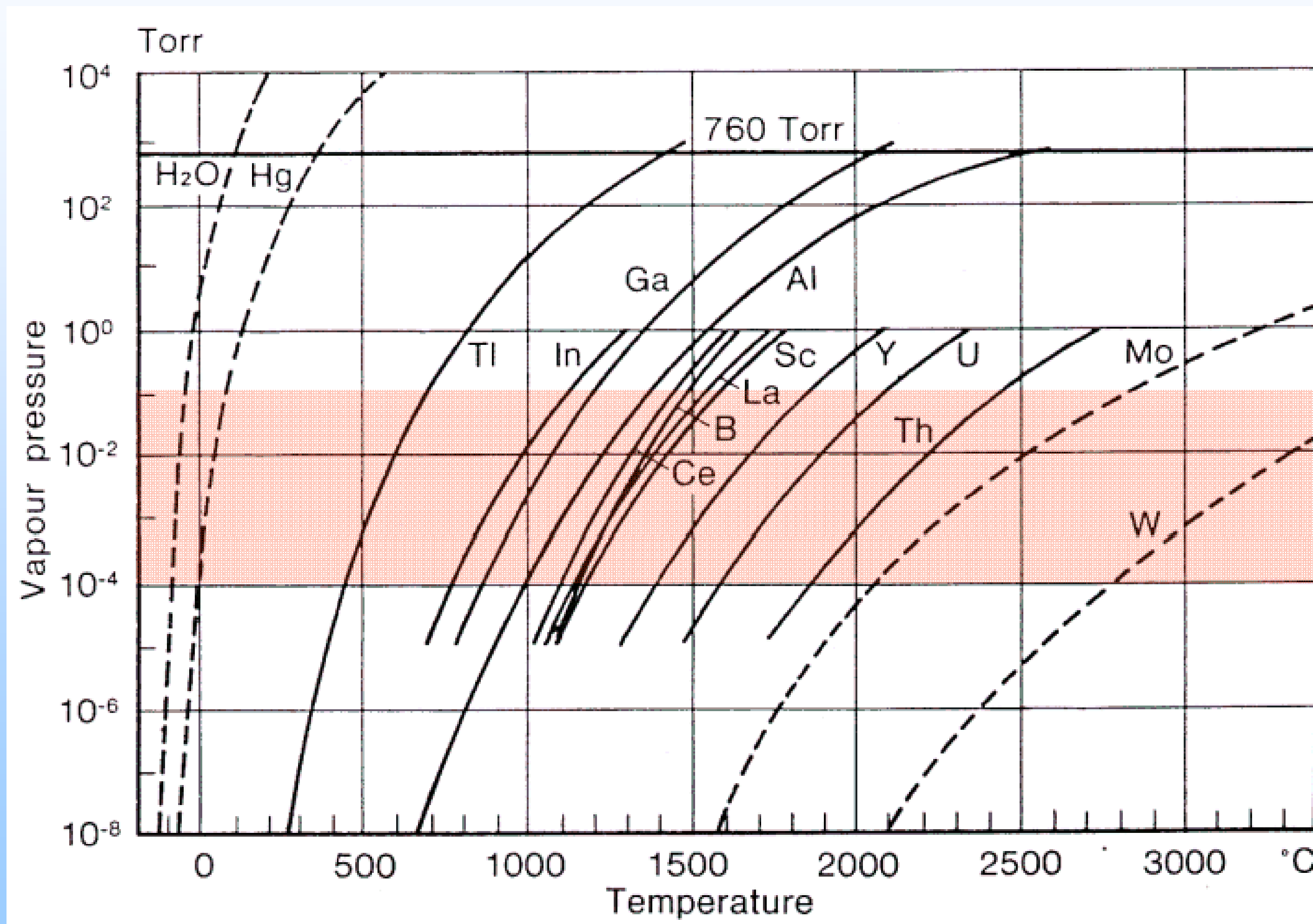
Boiling Point



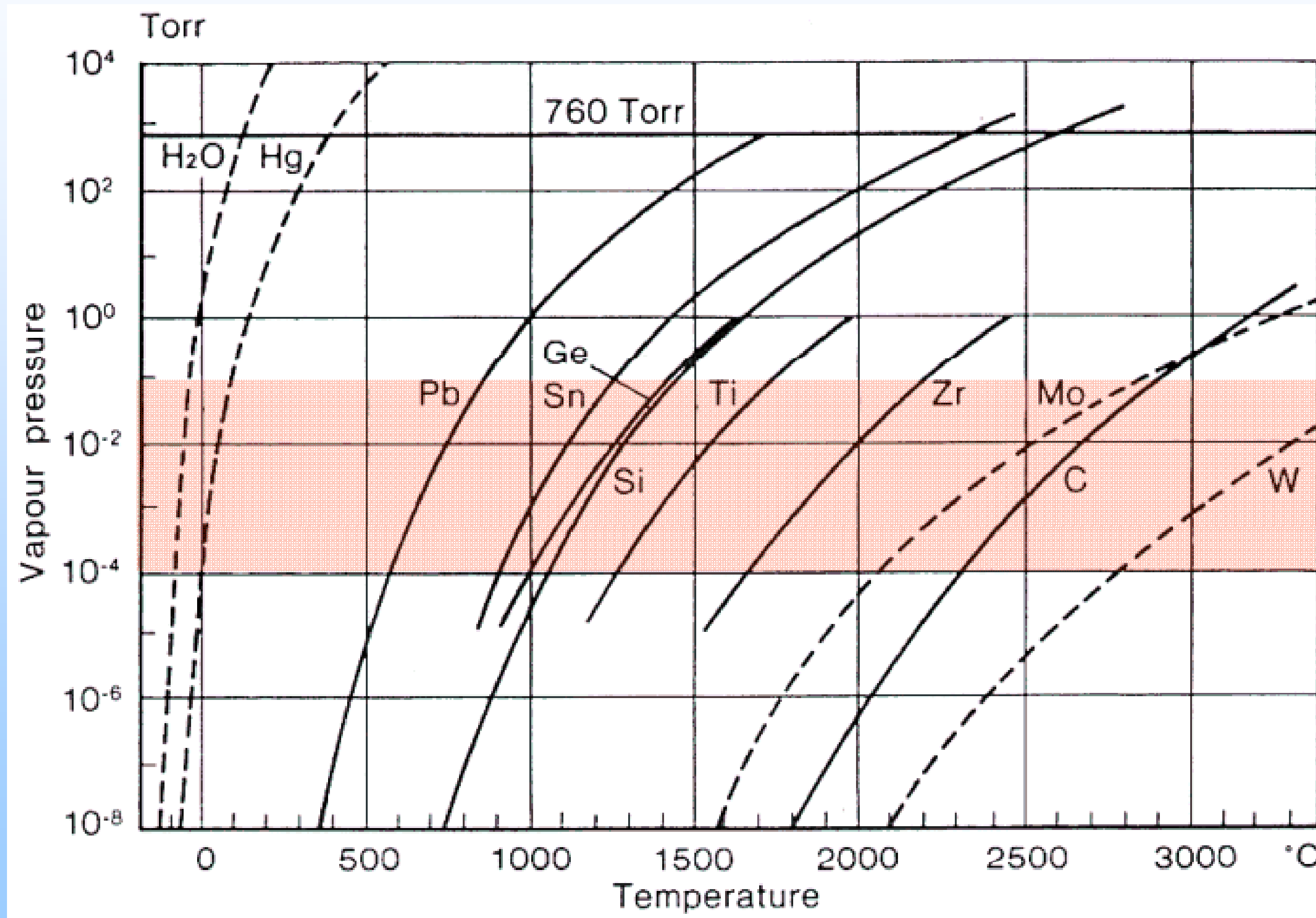
Saturated vapor pressure of 2. group elements dependent on temperature



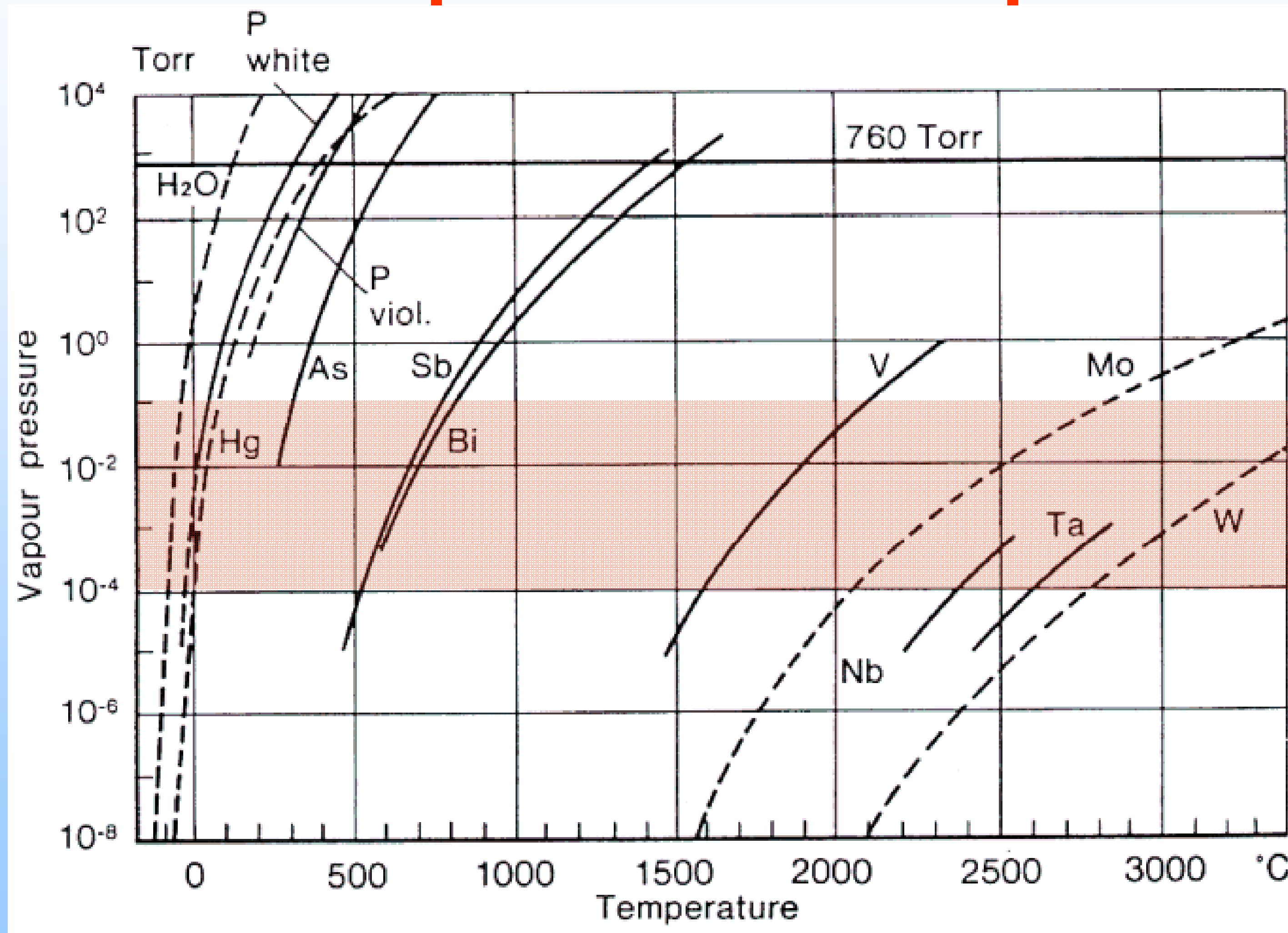
Saturated vapor pressure of 3. group elements dependent on temperature



Saturated vapor pressure of 4. group elements dependent on temperature



Saturated vapor pressure of 5. group elements dependent on temperature



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Metal	Data Temp. Range (°C)	t(°C) and W	$P_\mu =$					
			10^{-2}	10^{-1}	1	10	100	1000
Li	459–1080	t:	348	399	460	534	623	737
		W:	6.17 . 10^{-8}	5.93 . 10^{-7}	5.68 . 10^{-6}	5.41 . 10^{-5}	5.13 . 10^{-4}	4.84 . 10^{-3}
Na	264–928	t:	158	195	238	290	355	437
		W:	1.35 . 10^{-7}	1.29 . 10^{-6}	1.24 . 10^{-5}	1.18 . 10^{-4}	1.12 . 10^{-3}	1.05 . 10^{-2}
K	100–760	t:	91	123	162	208	266	341
		W:	1.91 . 10^{-7}	1.83 . 10^{-6}	1.75 . 10^{-5}	1.66 . 10^{-4}	1.57 . 10^{-3}	1.47 . 10^{-2}
Rb	..	t:	64	95	133	176	228	300
		W:	2.94 . 10^{-7}	2.81 . 10^{-6}	2.68 . 10^{-5}	2.55 . 10^{-4}	2.41 . 10^{-2}	2.22 10^{-2}
Cs	..	t:	46	75	110	152	206	277
		W:	3.77 . 10^{-7}	3.61 . 10^{-6}	3.44 . 10^{-5}	3.26 . 10^{-4}	3.07 . 10^{-3}	2.87 . 10^{-2}
Cu	969–1606	t:	942	1032	1142	1272	1427	1622
		W:	1.33 . 10^{-7}	1.29 . 10^{-6}	1.24 . 10^{-5}	1.18 . 10^{-4}	1.13 . 10^{-3}	1.07 . 10^{-2}
Ag	721–1000	t:	757	832	922	1032	1167	1337
		W:	1.89 . 10^{-7}	1.82 . 10^{-6}	1.75 . 10^{-5}	1.68 . 10^{-4}	1.60 . 10^{-3}	1.51 . 10^{-2}
Au	727–987	t:	987	1082	1197	1332	1507	1707
		W:	2.31 . 10^{-7}	2.26 . 10^{-6}	2.14 . 10^{-5}	2.05 . 10^{-4}	1.94 . 10^{-3}	1.84 . 10^{-2}
Be	899–1279	t:	902	987	1092	1212	1367	1567
		W:	5.11 . 10^{-8}	4.93 . 10^{-7}	4.74 . 10^{-6}	4.55 . 10^{-5}	4.33 . 10^{-4}	4.08 . 10^{-3}
Mg	736–1020	t:	287	330	382	442	517	612
		W:	1.22 . 10^{-7}	1.17 . 10^{-6}	1.12 . 10^{-5}	10.8 . 10^{-4}	1.02 . 10^{-3}	0.97 . 10^{-2}
Ca	527–647	t:	402	452	517	592	687	817
		W:	1.42 . 10^{-7}	1.37 . 10^{-6}	1.31 . 10^{-5}	1.26 . 10^{-4}	1.19 . 10^{-3}	1.12 . 10^{-2}
Sr	..	t:	342	394	456	531	623	742
		W:	2.20 . 10^{-7}	2.11 . 10^{-6}	2.02 . 10^{-5}	1.93 . 10^{-4}	1.82 . 10^{-3}	1.71 . 10^{-2}
Ba	1060–1138	t:	417	467	537	617	727	867
		W:	2.60 . 10^{-7}	2.51 . 10^{-6}	2.40 . 10^{-5}	2.28 . 10^{-4}	2.16 . 10^{-3}	2.03 . 10^{-2}
Zn	239–377	t:	208	246	290	342	405	485
		W:	2.15 . 10^{-7}	2.07 . 10^{-6}	1.99 . 10^{-5}	1.90 . 10^{-4}	1.81 . 10^{-3}	1.71 . 10^{-2}
Cd	200–260	t:	149	182	221	267	321	392
		W:	3.01 . 10^{-7}	2.90 . 10^{-6}	2.78 . 10^{-5}	2.66 . 10^{-4}	2.54 . 10^{-3}	2.44 . 10^{-2}
Hg	..	t:	−28	−8	16	45	81	125
		W:	5.28 . 10^{-7}	5.08 . 10^{-6}	4.86 . 10^{-5}	4.63 . 10^{-4}	4.39 . 10^{-3}	4.14 . 10^{-2}
B	..	t:	1687	1827	1977	2157	2377	2657
		W:	4.33 . 10^{-8}	4.19 . 10^{-7}	4.05 . 10^{-6}	3.89 . 10^{-5}	3.73 . 10^{-4}	3.55 . 10^{-3}
Al	1137–1195	t:	882	972	1082	1207	1347	1547
		W:	8.92 . 10^{-8}	8.59 . 10^{-7}	8.23 . 10^{-6}	7.88 . 10^{-5}	7.53 . 10^{-4}	7.10 . 10^{-3}

Table: Evaporation rates of some materials

Saturation pressure

p_μ [microns]

Evaporation rate

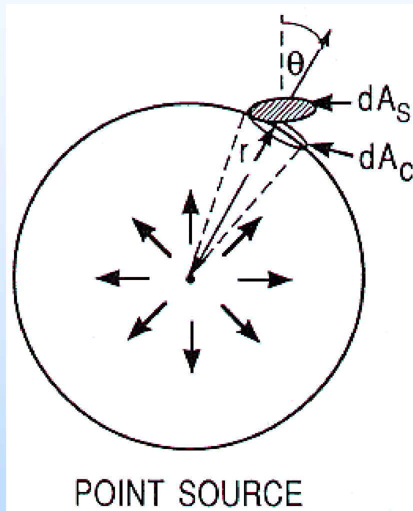
W [gcm^{-2}s^{-1}]

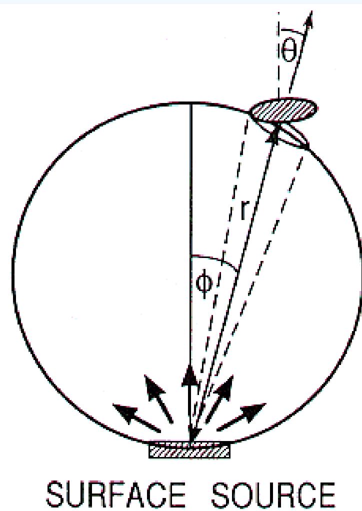
Geometry factor of evaporation

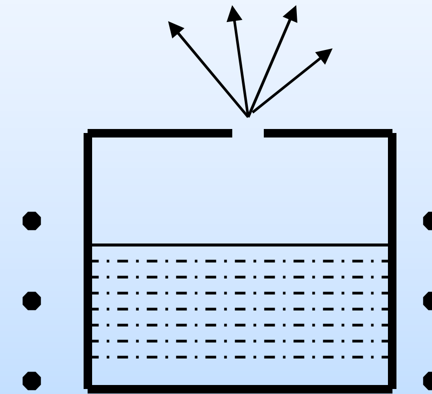
Evapoartion from a 1 D point source

Evapoartion from a 2 D surfac source

Knudsen - cell







Evaporated total mass:

$$\overline{M}_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt$$

$$\frac{d\overline{M}_s}{dA_s} = \frac{\overline{M}_e \cos\theta}{4\pi r^2}$$

$$\frac{d\overline{M}_s}{dA_s} = \frac{\overline{M}_e \cos\phi \cos\theta}{\pi r^2}$$

Γ_e : Evaporation rate

dA_s : Substrat surface unit

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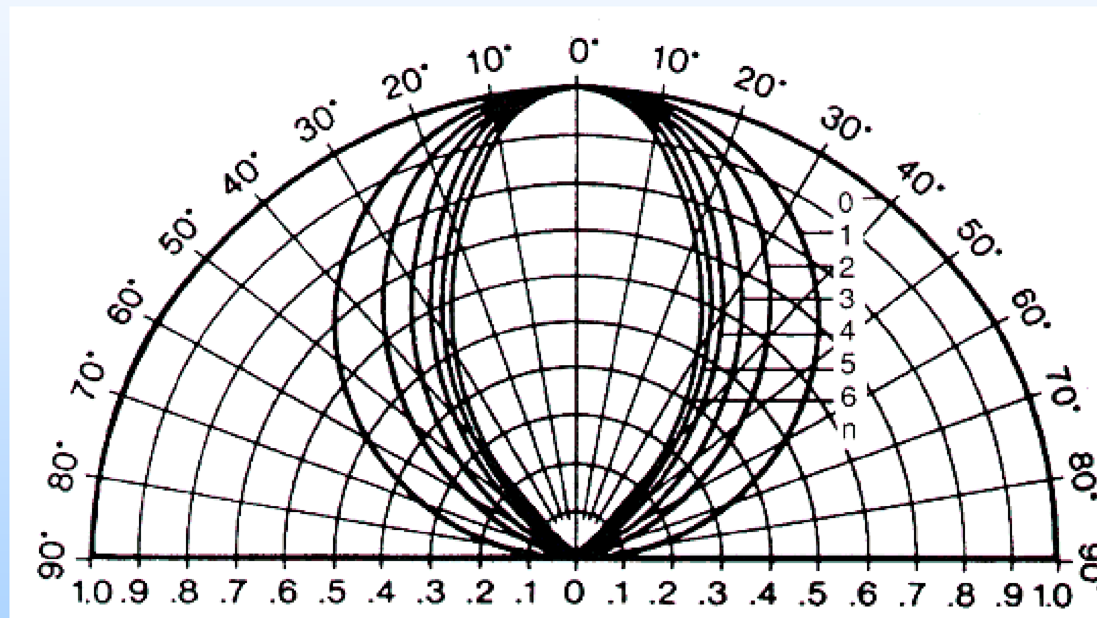
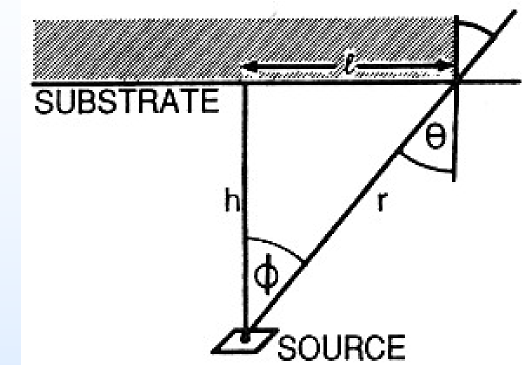
Geometry factor of evaporation

Calculated lobe-shaped vapor clouds of various cosine exponents



$$\frac{d\overline{M_s}}{dA_s} = \frac{\overline{M_e}(n+1)\cos^n\phi\cos\theta}{2\pi r^2} \qquad (n \geq 0)$$

Homogeneity of the film thickness



For point source

$$d = \frac{dM_s}{\rho dA_s} = \frac{\overline{M}_e \cos\theta}{4\pi\rho r^2} = \frac{\overline{M}_e h}{4\pi\rho r^3} = \frac{\overline{M}_e h}{4\pi\rho\left(h^2 + l^2\right)^{3/2}}$$

The thickst deposittion d_0 is at $l = 0$

where

$$d_0 = \overline{M}_e / 4\pi\rho h^2$$

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

Homogeneity of the film thickness

For the surface source $\cos\theta = \cos\phi = h/r$

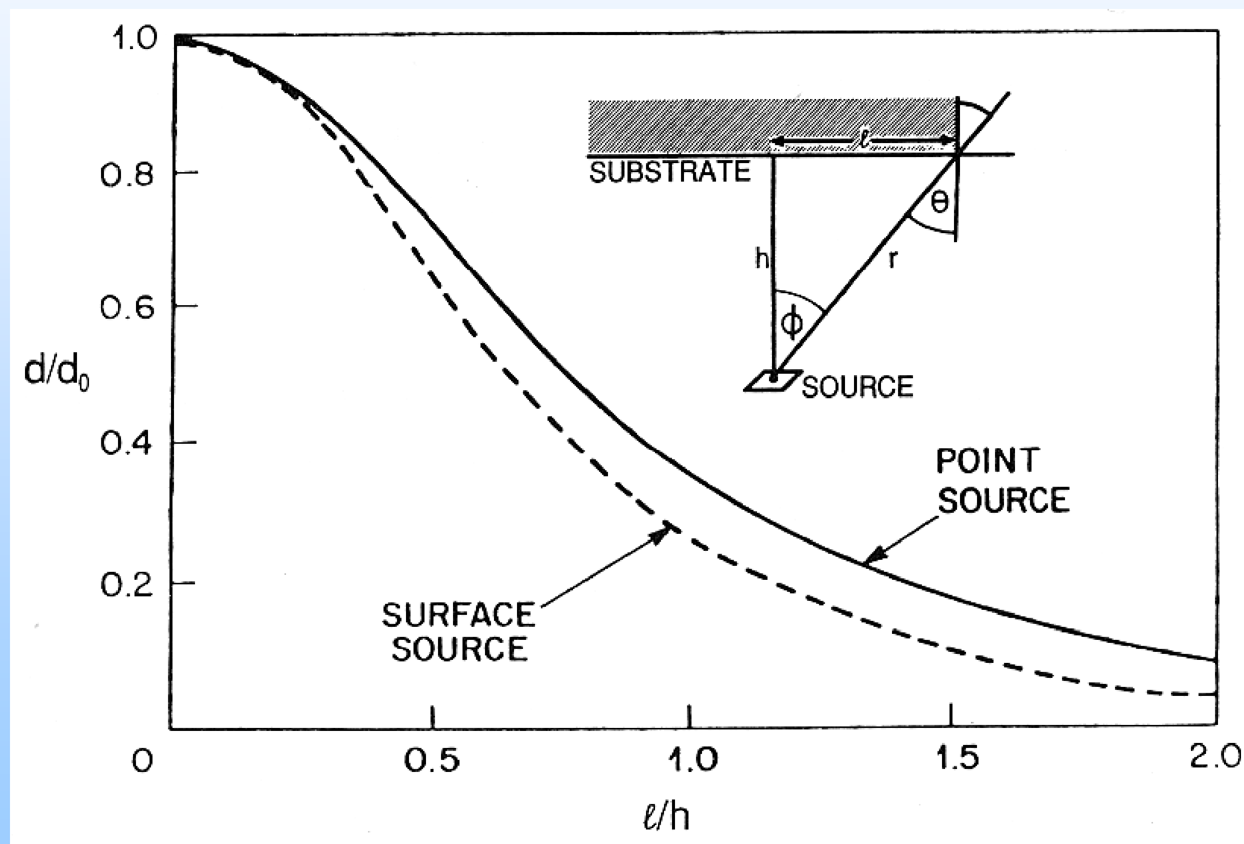
$$d = \frac{\overline{M}_e \cos\theta \cos\phi}{\pi\rho r^2} = \frac{\overline{M}_e}{\pi\rho r^2}\frac{h}{r}\frac{h}{r} = \frac{\overline{M}_e h^2}{\pi\rho\left(h^2 + l^2\right)^2}$$

Normalized upon $d_0 = \overline{M}_e / \pi\rho h^2$

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

Homogeneity of the film thickness

Homogeneity of the film thickness for point and surface sources. Evaporation geometry on parallel, plate substrate.



Possibility of Evaporation

- Resistance/Boat heater (Electrically heated boats)
- Knodsen cells
- Electron beam evaporation

States of evaporated atoms and molecules

Metals: in most cases single atoms

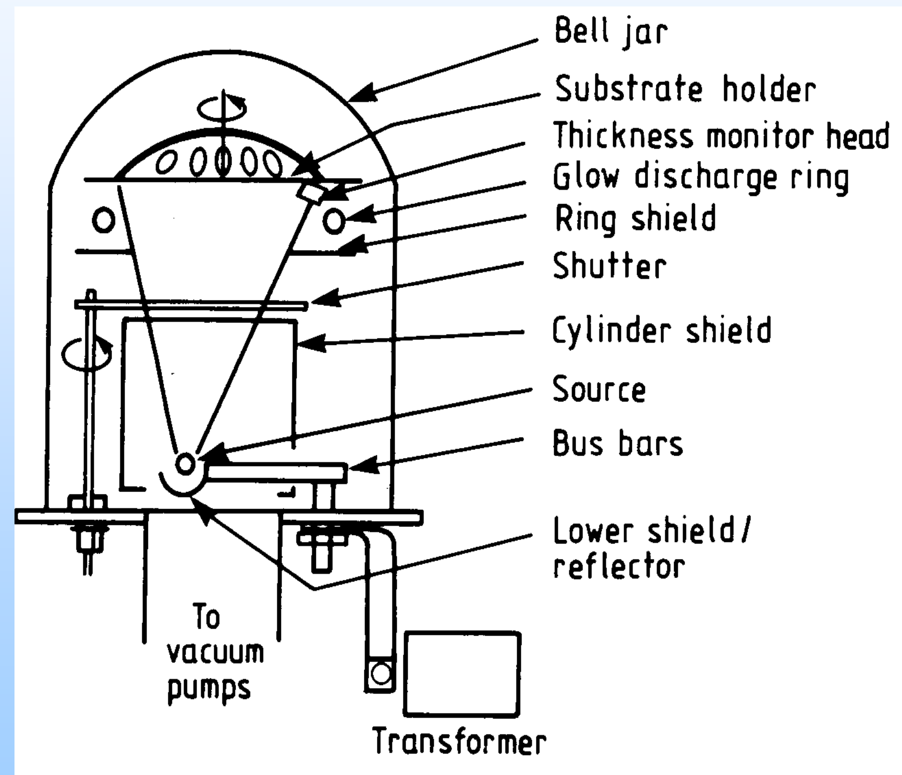
Metalic alloys: single atoms. For example, Fe-Ni, Ni-Cr

Semiconductors: some times also clusters with 2 or more than 2 atoms will be evaporated.

For example, Sb ⇨ Sb_4 + Sb_2; As ⇨ As_4 + As_2; P ⇨ P_4 + P_2, Bi ⇨ Bi_2; Te ⇨ Te_2

Resistance Evaporation

- First practical use for thin film deposition
- Reliable and economic
- Competitive with EBE and sputtering in some applications
- Multilayer resistance source deposited films use in most production dichroic light reflectors - examples of cost efficiency, modern technology.



Sources

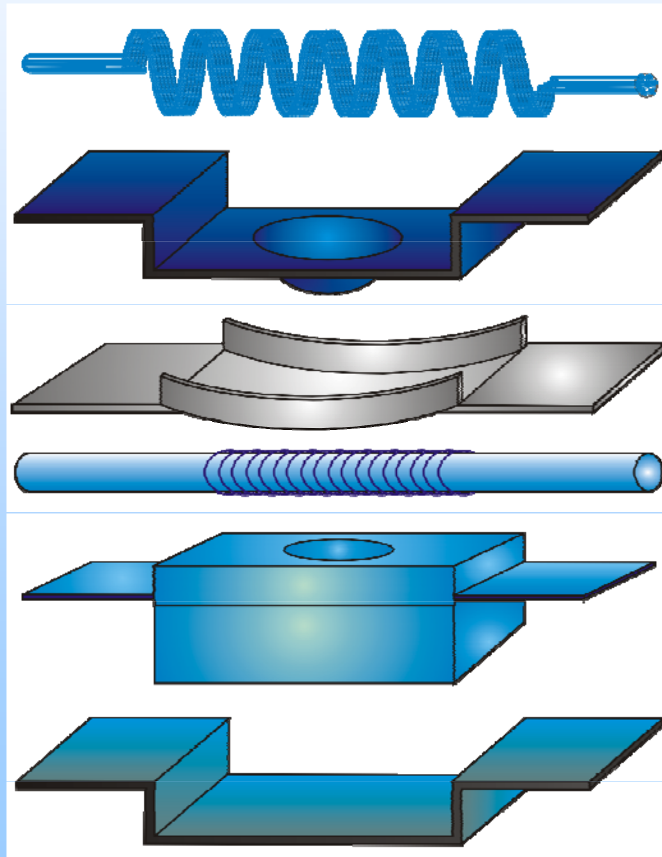
- Resistance heated refractory metal source is the heart of each evaporation system
- Source - evaporant heater and container - frequent failure of evaporant system

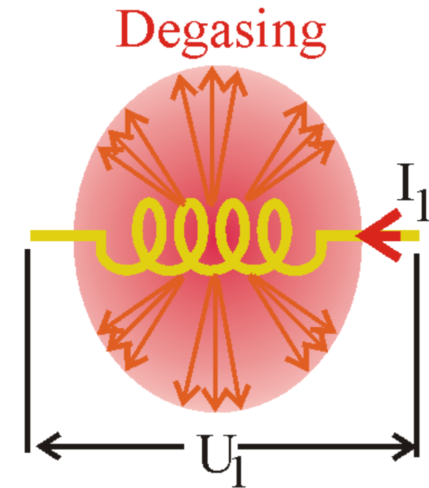
Selection of source

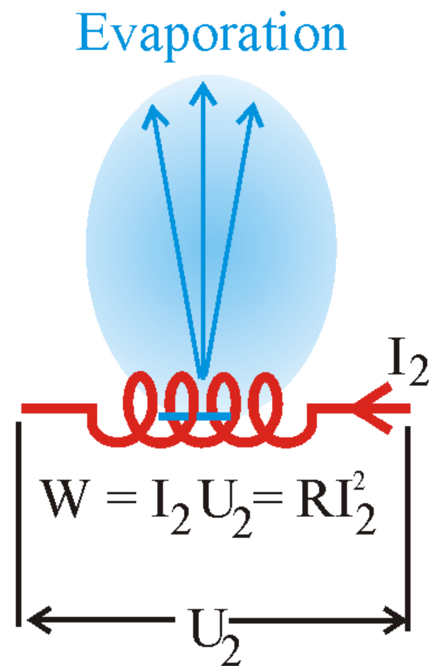
- Tabulated data - starting point in selecting source
- Selected source should meet the following requirement
  - Evaporant compatibility: Al, Au, Fe, Pt dissolve refractory metals - Mo Ta, W.
  - Availability of power

Design of Sources

- Coils
- Boats
- Special constructions



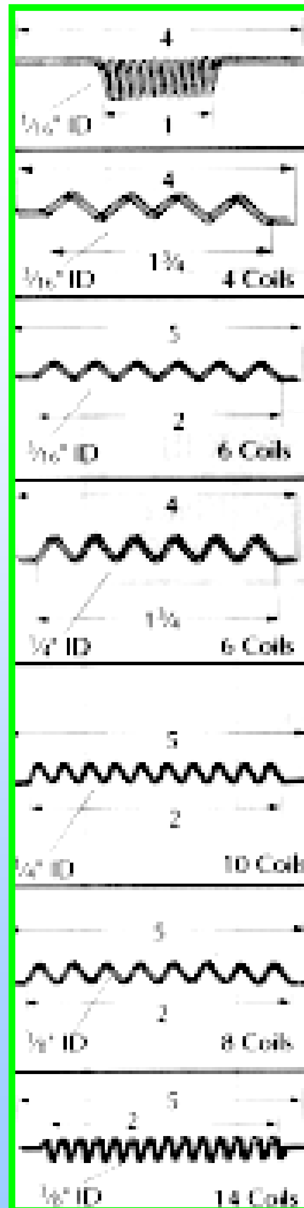


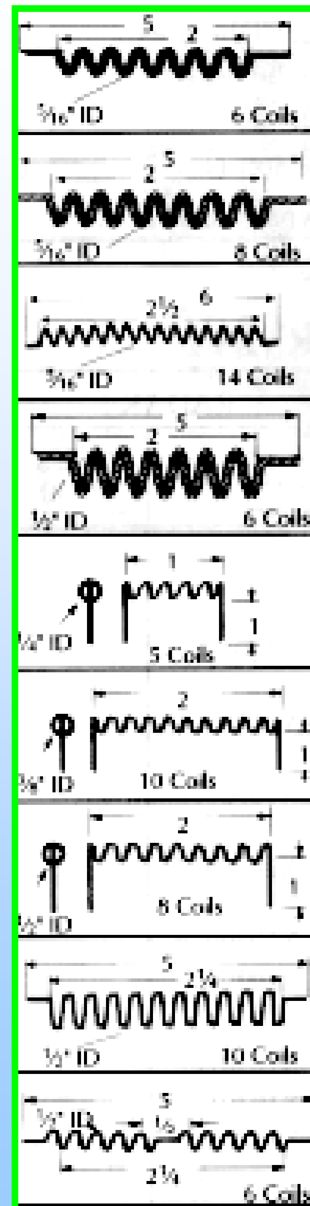


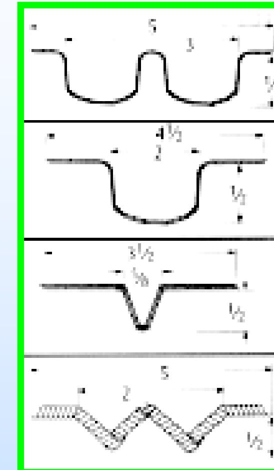
Coils

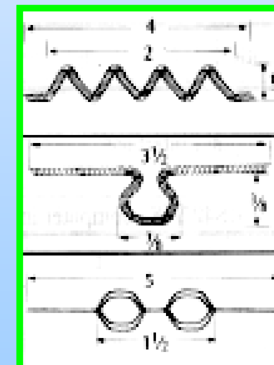
- W-wire supports evaporant
- Isotropic emitter: low capacity and cost: Used in large drum coaters for decorative metalizing
- Central position permits the upward and downward emission
- Commonly used for Al; Less for Au, Ag, Cu, Sn
- Efficient coil evaporation for e.g. Al requires the Al charge be less than 10% of the coil weight.
- To minimize dripping of melting Al: Rapid increase to the evaporation temperature 1200 - 1500 ^{o}C
- Heavy multistrand wire coil have the highest capacity - more power
- Conical coils - for small droplets or pieces of evaporant
- Rod sources - classified in the coil category
- Rod with overwind wire increases lifetime
- Rod is preferred over coils particularly for difficult materials (Ni and Iconel)

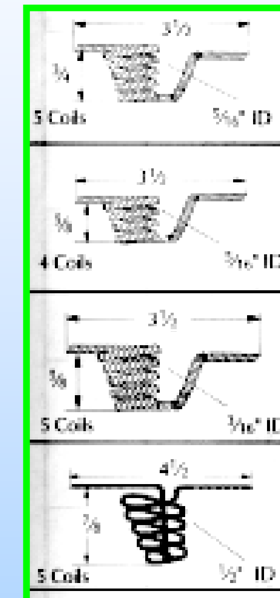
Coil Sources



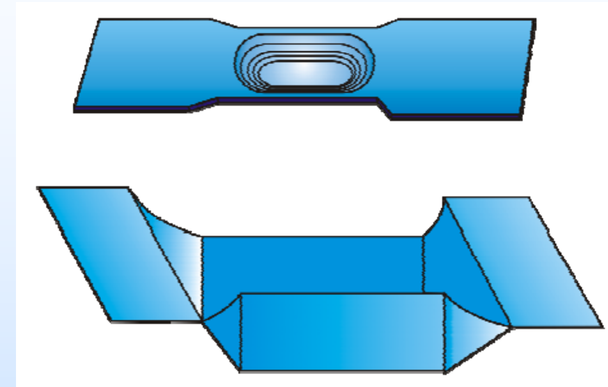






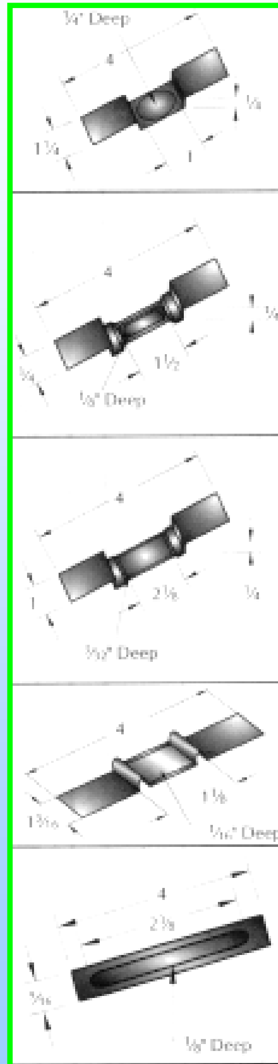


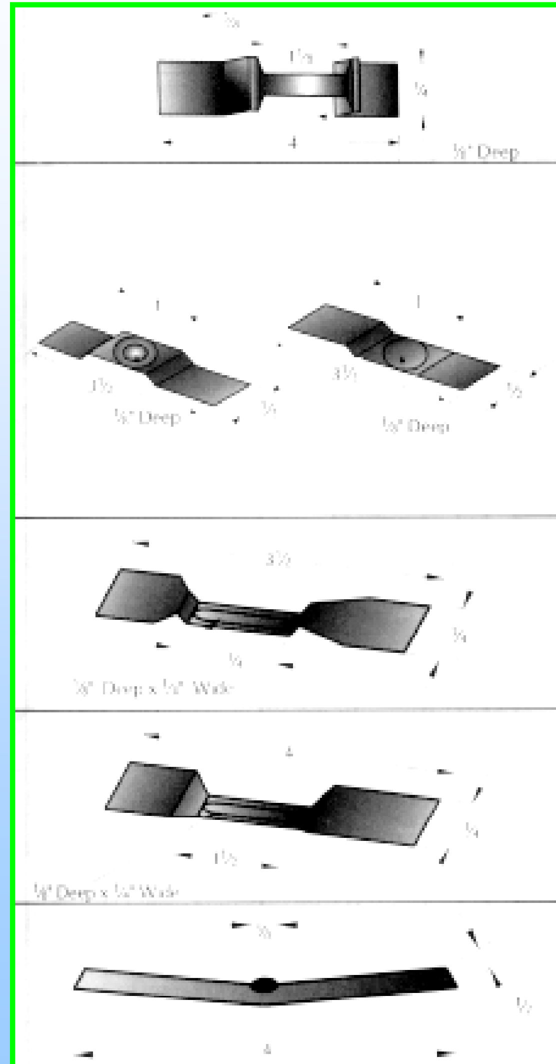
Boats



- Hold evaporant in dimples or folds
- Heated by electric current
- Available in an endless range of sizes and shapes
- Must operate at temperatures considerably above that required to evaporate the material.
- This temperature is principal limitation of the capability of the boats
- Solubility of evaporant and boat materials
- Alloying thins and embrittles the boat leading to cracking
- In some cases (Pt) the melting point of the boat/evaporant alloy is so much lower than that of the pure refractory boat.

Boats





Special Boats

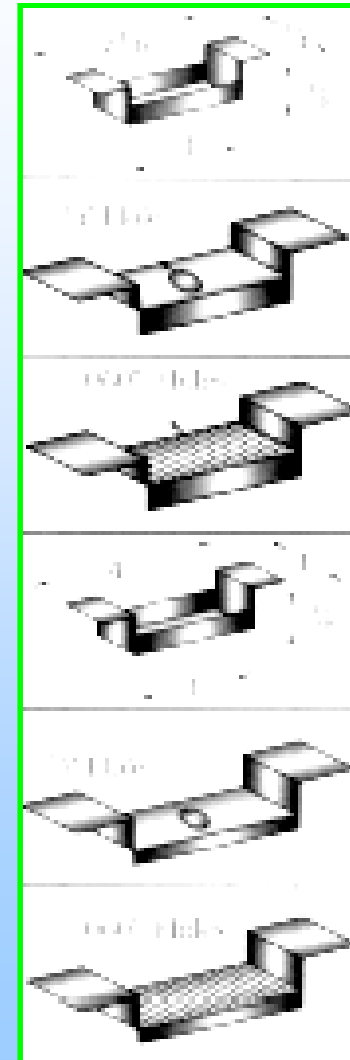


Table: Melting Points of Pure Refractory Metals and their Alloys

Material	Melting Point [^{o}C]	Material	Melting Point [^{o}C]	Material	Melting Point [^{o}C]
W	3410	Mo	2610	Ta	2996
W_2C	2860	Mo_2C	2687	TaC	3880
WO_3	1473	MoO_3	795	TaN	3360
WS_2	1250	$MoSi_2$	2050	Ta_2O_5	1872
				TaS_2	~1300

Alloying can be minimized

- Selecting the most suitable materials for the boats
- Coating the boat with inert film, usually Al_2O_3 - requires higher boat temperatures - accelerates cracking
- Making massive boat - allowing the saturation of the surface with evaporant (0.5 - 1 mm thick boats) –expensive, more difficult to make it.

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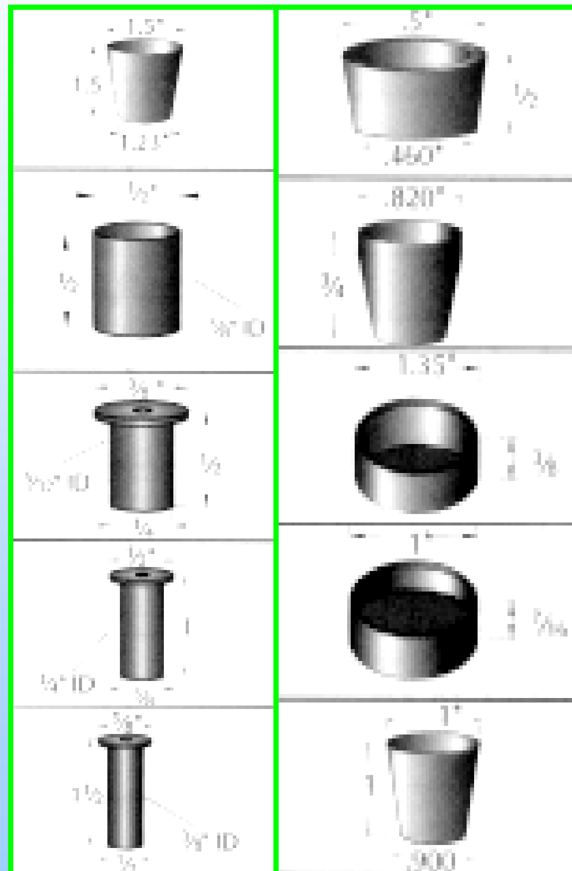
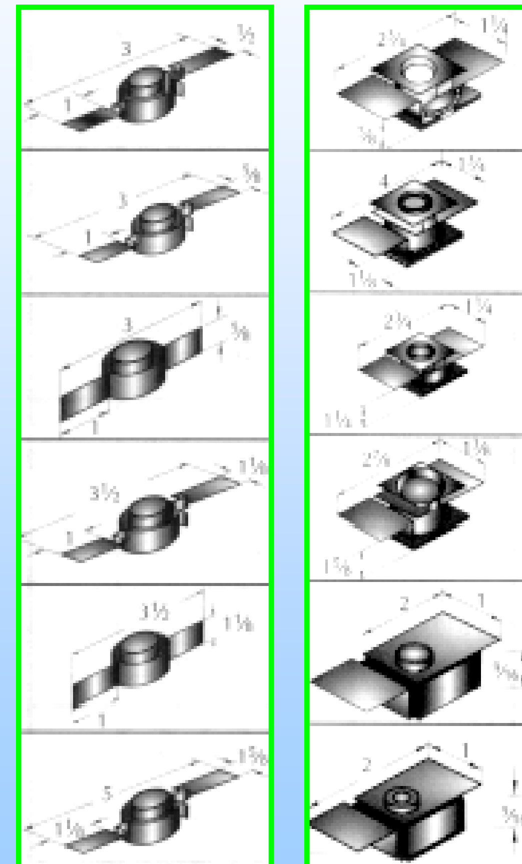
Crucibles



Crucible Heaters

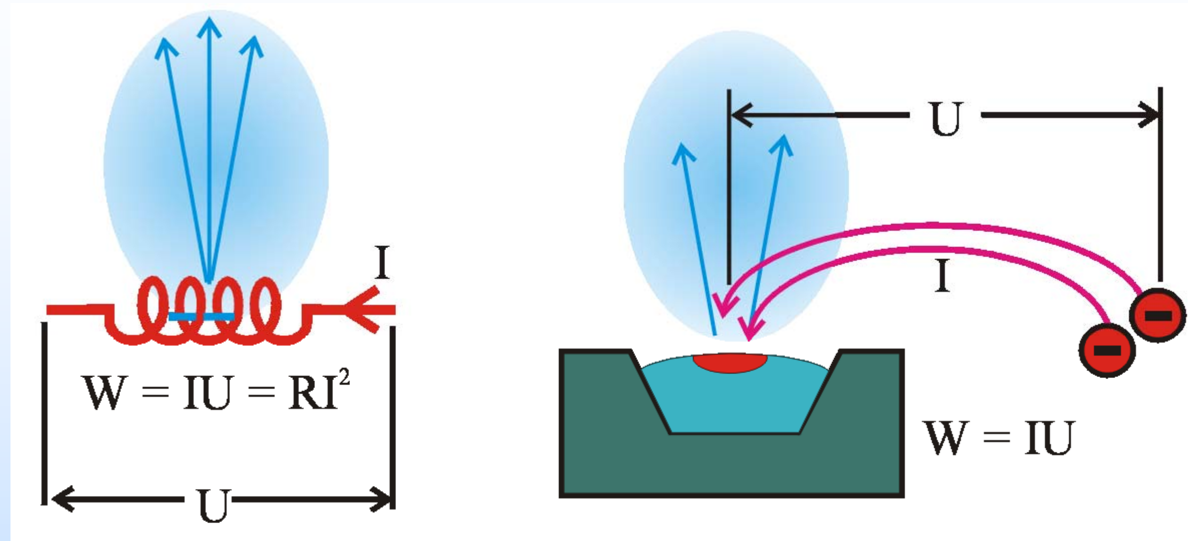


Electron Beam Evaporation

Applications

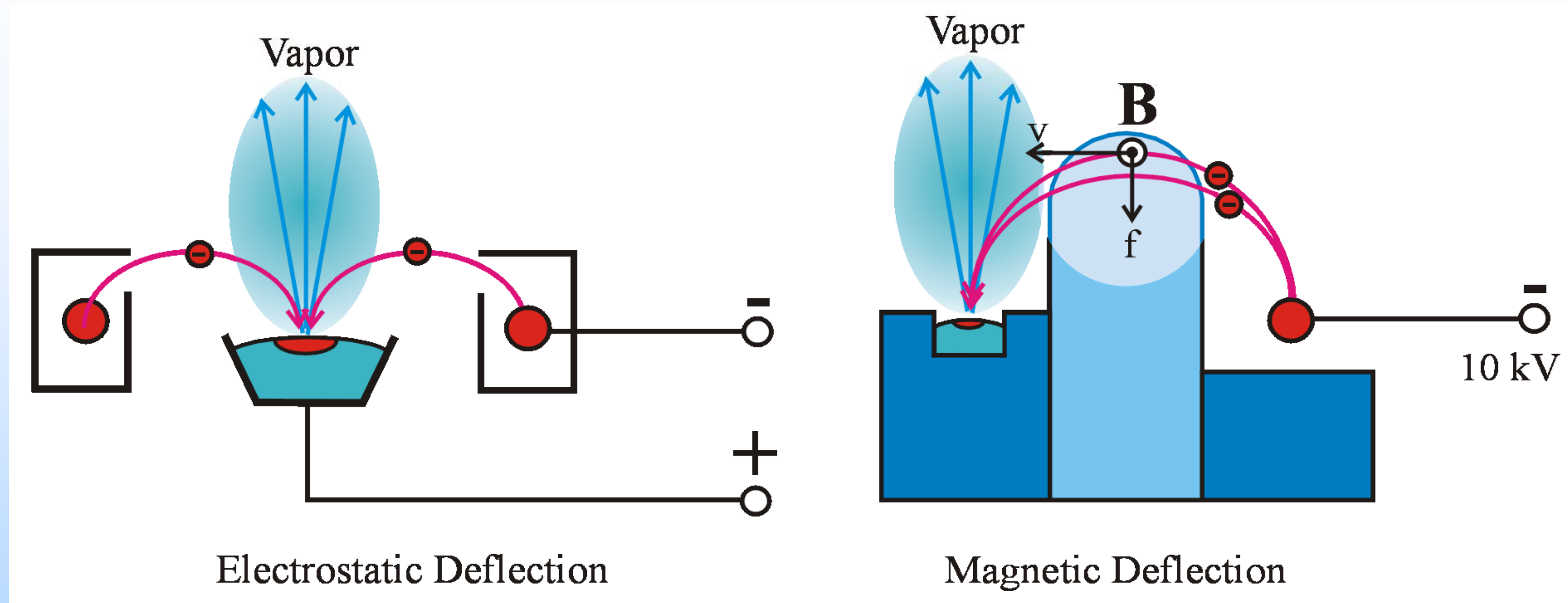
- Semiconductor industry
  - Compatibility
    - Planar magnetron
    - MBE - doping
  - High deposition rate
  - Easy control
- Optical coatings
- Multilayer coatings

Properties



- E-beam evaporation source - thermal evaporator
- It differs from resistance source
- Energy is supplied to the top of the evaporant - e-beam
- Evaporant is in a water cooled hearth
- Very local heat dissipates by radiation and conduction
- Reaction with hearth is mostly prevented
- EBE is universal source
- Allows deposition of materials with high melting points

Design



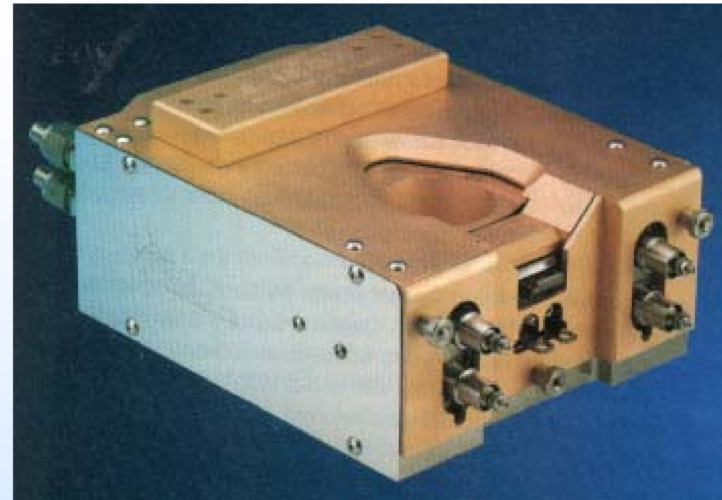
- EBE proposed by Holland
- e-beam bending by
  - E-field
  - B-field

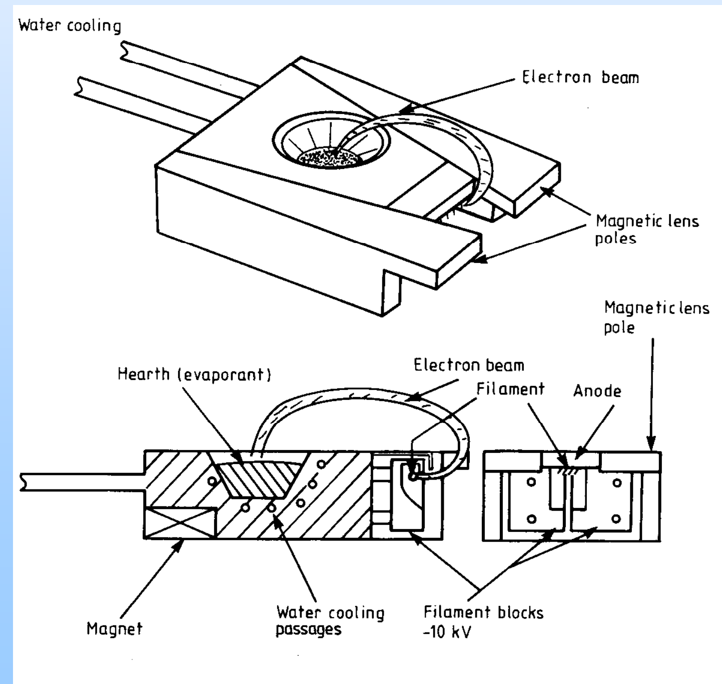
Design

- e-beam bending in 270º by B-field

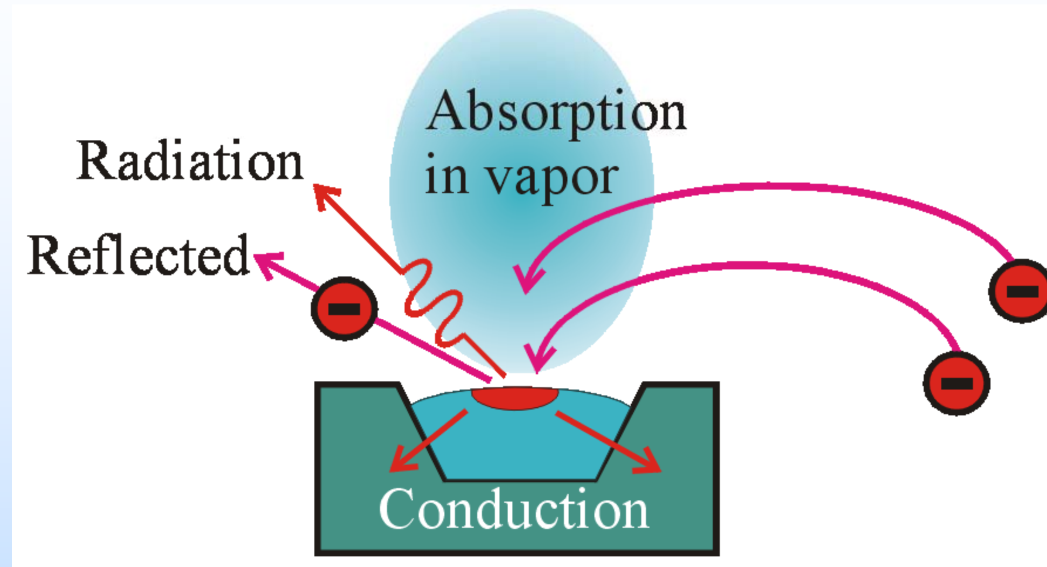
Three Fundamental Parts

- Electron beam gun
- Magnetic deflection lens
- Water-cooled evaporation hearth





Energy Supply and Heat Dissipation



- Phase change of evaporant
- Conduction to the hearth supply energy
- Radiation
- Reflection of e-beam from evaporant
- 10 keV e-beam gives up its energy at the surface within a small fraction of a millimeter
- Evaporant charge should provide stable heat dissipation at any stage of evaporation

Parameters of Power Supplies

• High voltage:	5 - 10 kV DC
• E-beam current:	0 -1.5 A DC
• Filament current:	0 - 40 A AC
• Filament voltage:	0 - 6 V AC
• Position magnet voltage:	-2 to +2 V DC
• Position magnet current:	0 - 3 A DC
• Emission control voltage:	0 to - 10 V DC

Practical Evaporation

• Saturated vapor pressure at least	p ~ 10^{-1} Torr
• For high evaporation rate	p ~ 10 Torr
• E-beam parameters	10 keV/1.5 A
• E-beam impact area:	0.25 - 1.0 cm^2
• Maximum power density:	60 kW/cm^2

Evaporation Guidance

- Ideal evaporants: Ag, Al, Au, Cu; Evaporation starts at 10^{-4} Torr
- Evaporation rate increases with increasing energy until the evaporant pressure over the beam impact point reaches viscous flow (~10^{-1} Torr)
- As the T-change is small from the point of the first evaporation to instability, (for Al 1245 K at 10^{-4} to 1640 K at 10^{-1} Torr), heat losses by conduction to the hearth and radiation do not increase rapidly - evaporation rate increases exponentially with the increase in power until limited by vapor density above surface
- Added energy is absorbed by evaporant cloud - limiting the further increase in evaporation rate
- Evaporation rate can further increase at constant or increased power only by increasing the e-beam impact area, thereby reducing the power density

Evaporation Characteristics

- Evaporant quantity as little as 1 cm^3
- The most important steps are
  - Selection of evaporant form
  - Conditioning of the evaporant

Conditioning of Evaporant Consists of Following

- Closed shutter
- Outgassing of evaporant
- Slow increase in power over several minutes to 1-1.5 time to the level desired before opening shutter
- If melting material evolves large quantity of gas, pressure rise above maximum acceptable level (4×10^{-5} Torr)
- Outgassing very slowly at high power

Evaporation of alloy and compound films

- Alloys/mixtures of materials - wide technical applications
- Alloys/mixture - difficult to deposit
- No deposition method for preserving the alloy/mixture composition

Evaporation

- Evaporation – alloy constituents (with rare exceptions) evaporate at different rates – differences in vapor pressures – results in films with variable composition.
- Evaporation of the alloy constituents from individual sources is versatile but difficult to control - the sources cannot be co-located.
- Interactions of the components of alloys during evaporation are complex
- Evaporation of alloys is practical for materials with similar vapor pressures. Alloys never evaporate with exact composition unless vapor pressures of the components and alloy are identical.
- Practical alloy evaporation requires special composition of evaporant alloy
- Often source replenishment is required - to maintain constant film composition.

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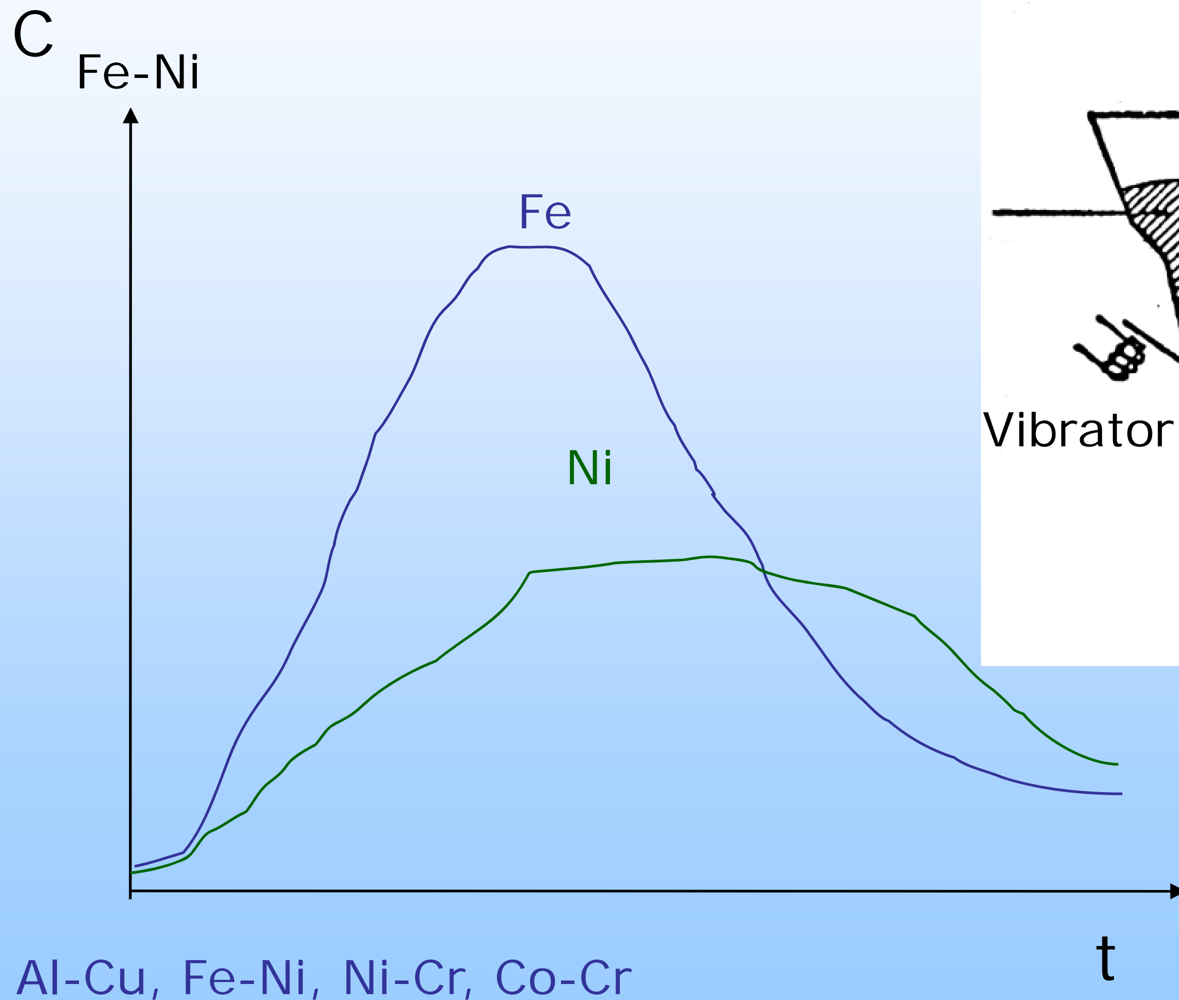
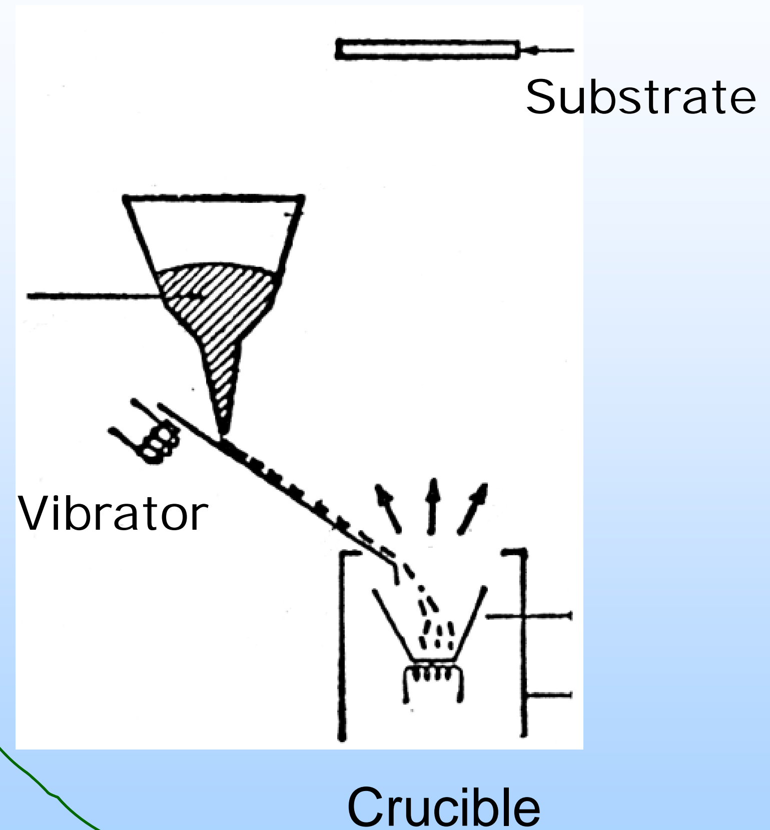
Evaporation of alloy and compound films





Al-Cu, Fe-Ni, Ni-Cr, Co-Cr

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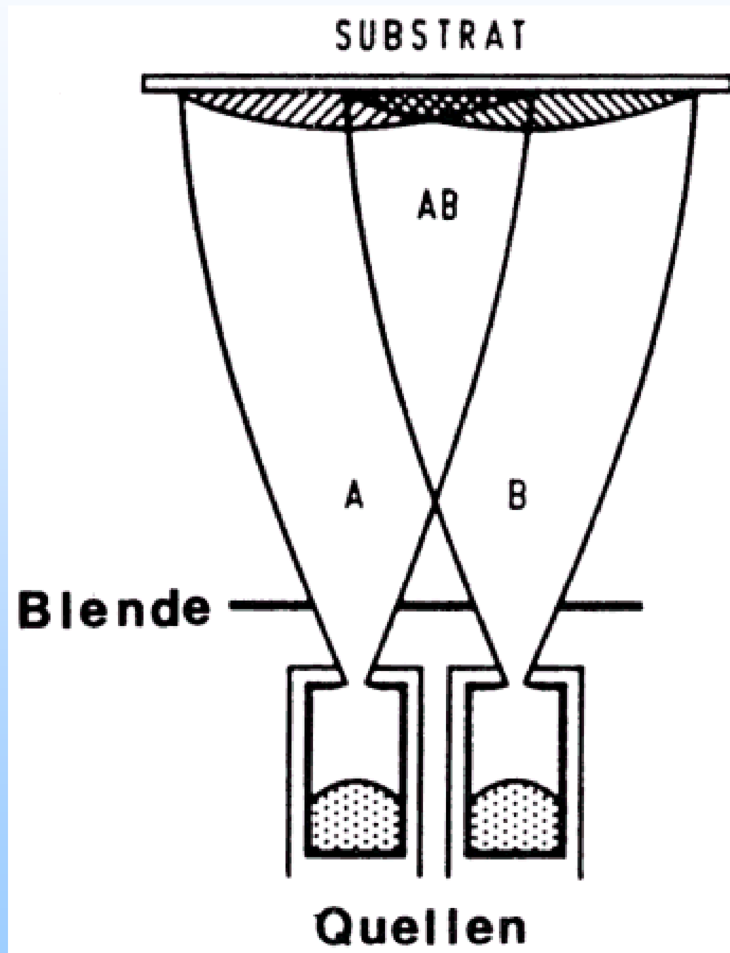
Evaporation of alloy and compound films



AB – Legierung

If the evaporation rate A > B

A_xB – Film x > 1

Reactive Evaporation RE

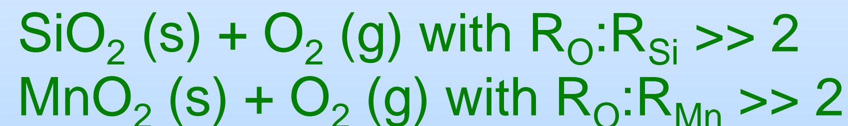
Evaporation from dissociated compounds

e.g.

SiO_2 (source) → SiO_x (film) + O_2 (g) with $x<2$

MnO_2 (source) → MnO_x (film) + O_2 (g) with $x<2$

For reactive evaporation:



SiO_2 (s) + O_2 (g) with $R_O:R_{Si} >> 2$

MnO_2 (s) + O_2 (g) with $R_O:R_{Mn} >> 2$

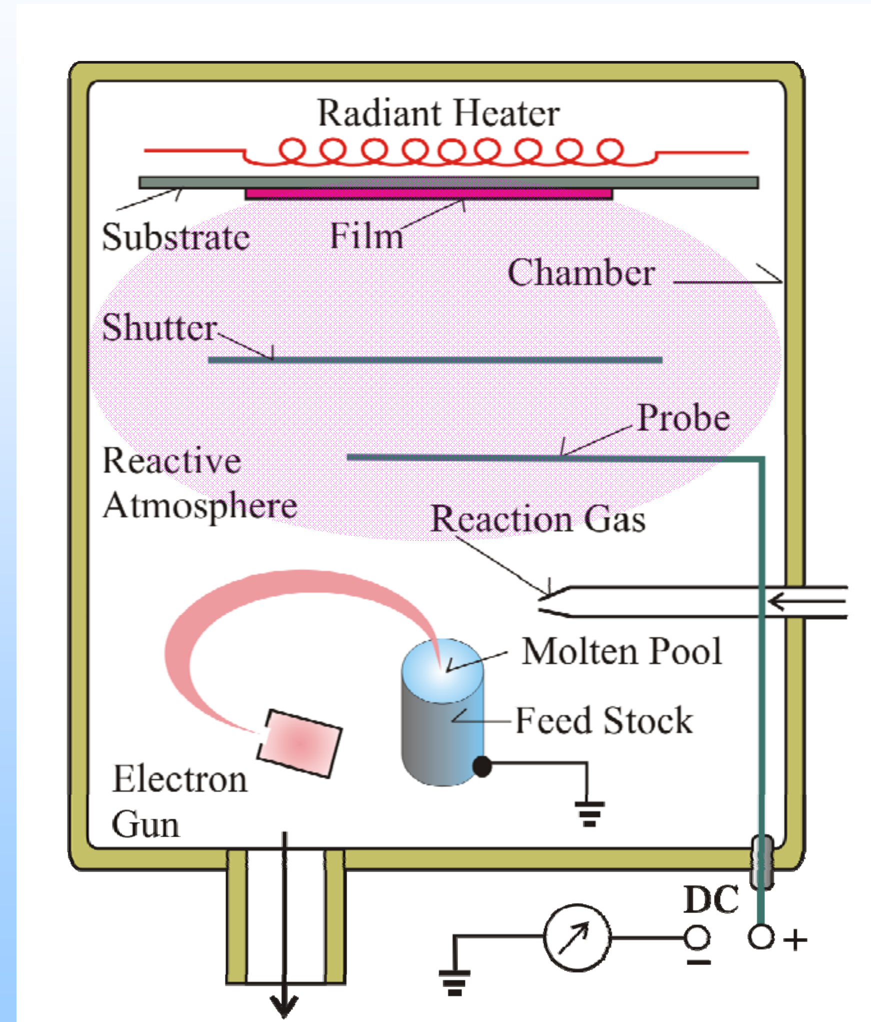
Problem: P_{O2} is too large →

Activated Reactive Evaporation (ARE)

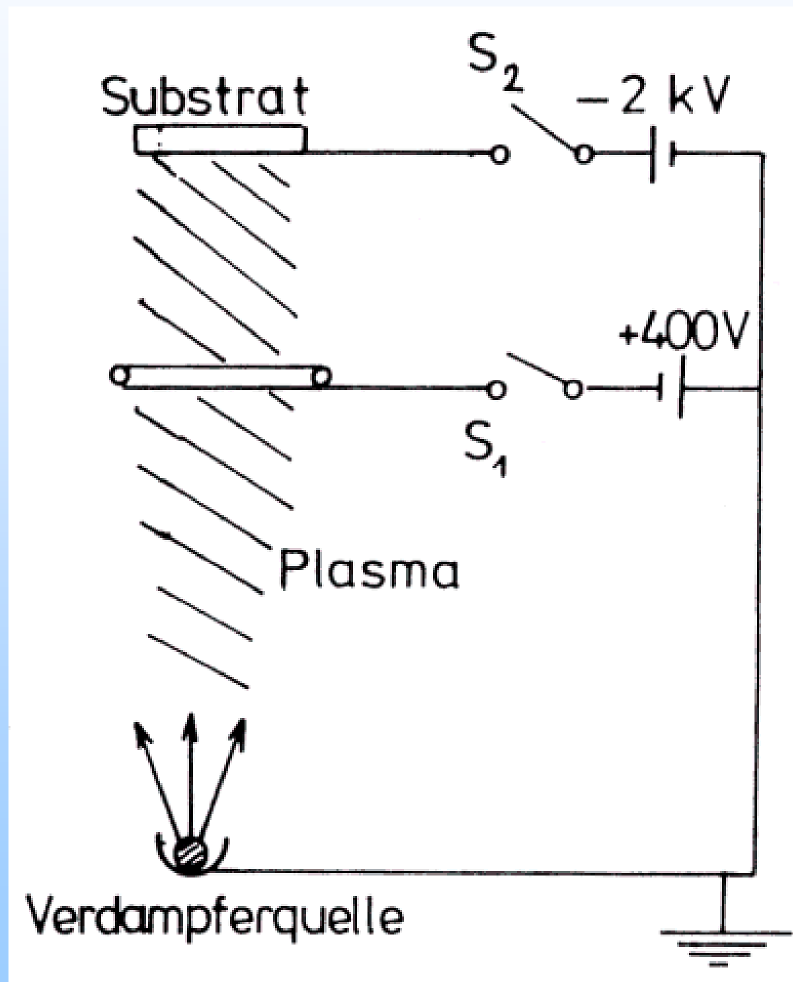
Hard coatings, e.g. TiC, TiN, ZrC, VC, NbC, HfC, HfN, Al_2O_3

Activated Reactive Evaporation (ARE)

- Metal evaporated by an EBE source reacts with a reactive gas plasma and deposit as a compound film
- Plasma is generated between the grounded chamber wall and probe with positive potential
- DC voltage/Probe currents = 40 - 170 mA/20 – 80 V.
- Reactive gases, as in sputter deposition - listed in Table
- Pressure during deposition ~ $10^{-3} – 10^{-4}$ Torr.



Biased Activated Reactive Evaporation (BARE)



BARE: ARE with Bias Potential on Substrate

V_b = -1 ~ -2 kV

S1 and S2 closed

For TiN: N^+ ions accelerated

→ Increase of nitrogen content

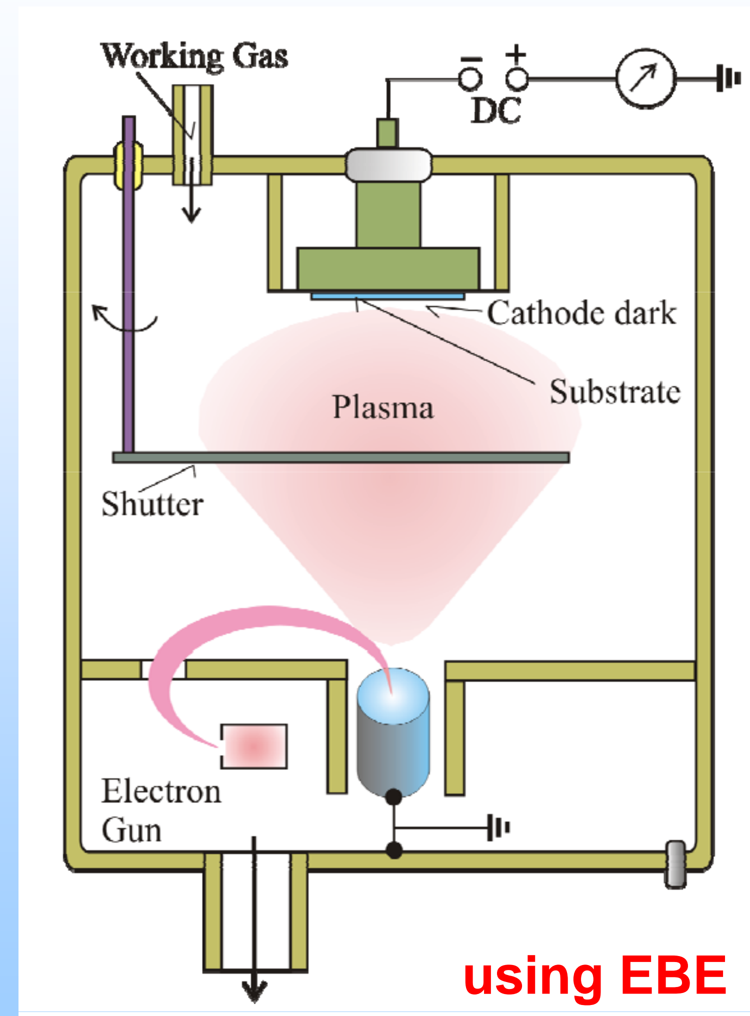
→ At a deposition rate from 20 to 60 µm/h, and T = 600 - 800°C well adhesive TiN films can be obtained.

Ion platting - Glow discharge

V_b (Cathode) = -2 ~ -5 kV

Gas pressure = $10^{-1} – 10^{-2}$ mbar

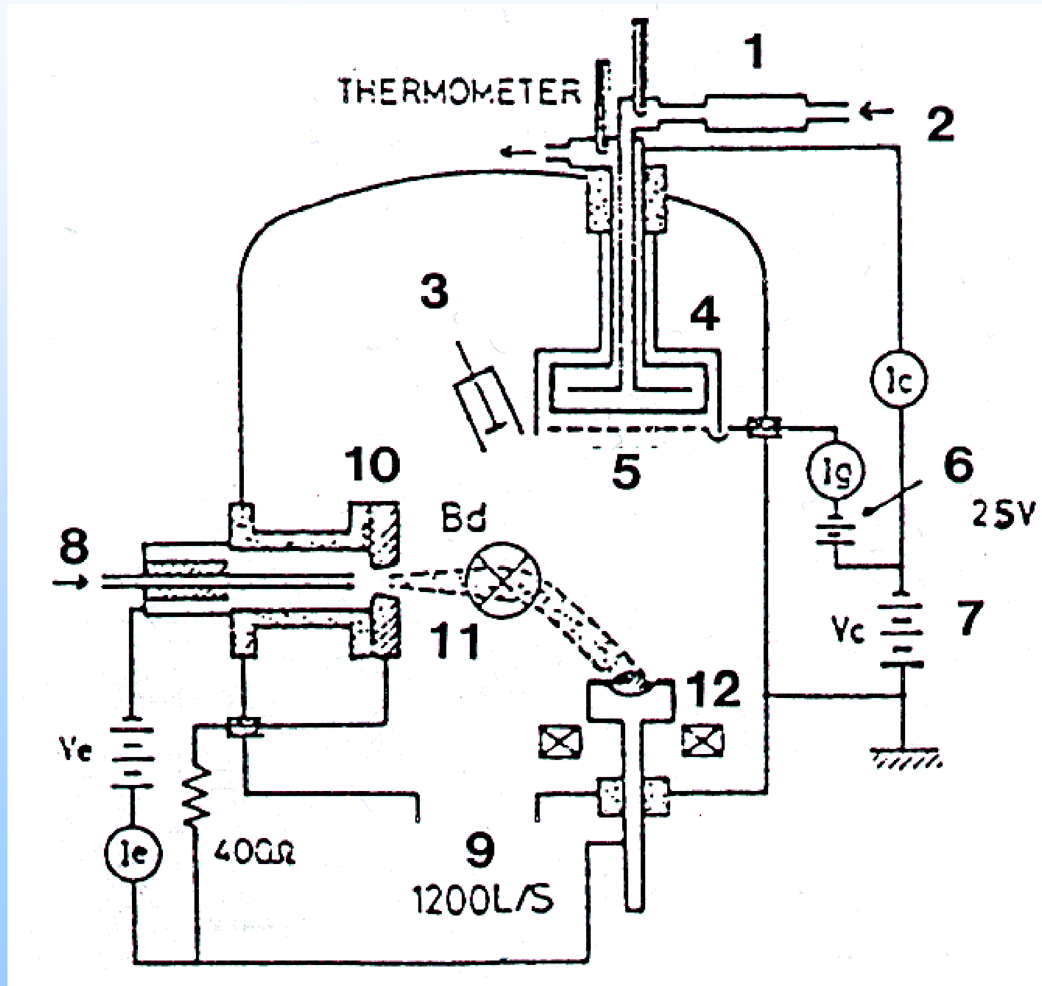
Advantages:
- Substrate cleaning
- Good adhesion
- Reduction of shadowing effect (Ion scattering at high pressure)



TiN, TiC films

For same film quality substrate temperature reduction

Ion platting –
Hollow cathode discharge (HCD) method



1. Thermometer
2. Substrate cooling
3. Thickness monitor
4. Shutter
5. Grit
6. Grit potential
7. Substrate voltage
8. Argon
9. Pump
10. HCD canon
11. Magnet
12. Source

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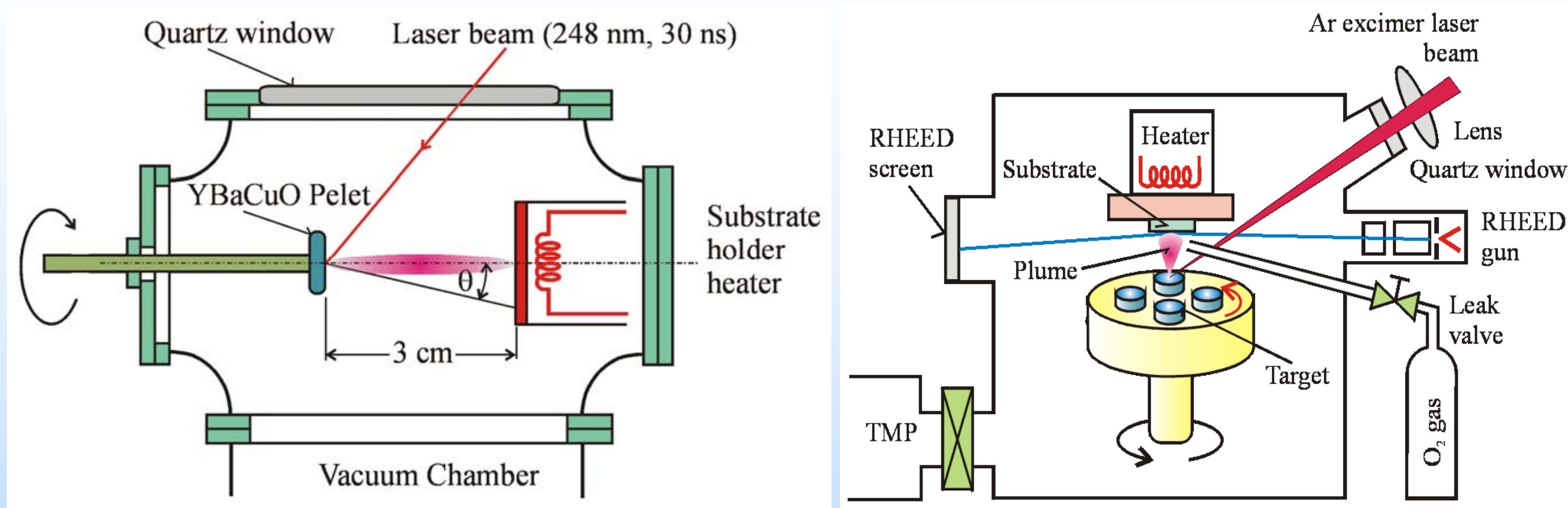
Laser Ablation



- Laser ablation - irradiation of the target by a focused laser beam
- A luminous cloud "plume" along the normal to the target
- Ablated materials are transferred to substrates
- Film grows - with nearly the target composition
- 30 –50% clusters ionized
- Fast (10^6 cm s^{-1}) and slow (10^3 – 10^4 cm s^{-1}) components

Growth by two kinds of particles evaporated by LA

1. Droplets deposition by LA

- The most important issue to solve for the film application prepared by LA
- Greatly affected by wavelength of the pulse laser employed

  Examples: Superconducting $YBa_2Cu_3O_x$ (YBCO) films
  - 1064 nm laser - Surface morphology rough - Large droplets
  - UV laser (355 nm) - Smaller droplets
- Wavelength is crucial parameter for clarifying the ablation mechanism
- Improvement - Ejected clusters are decomposed efficiently as a result of irradiation by a second laser beam with a shorter wavelength

2. Outgrowth cause by the recrystalization of films

The outgrowth occurs for other techniques as well

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Laser ablation - attractive technique

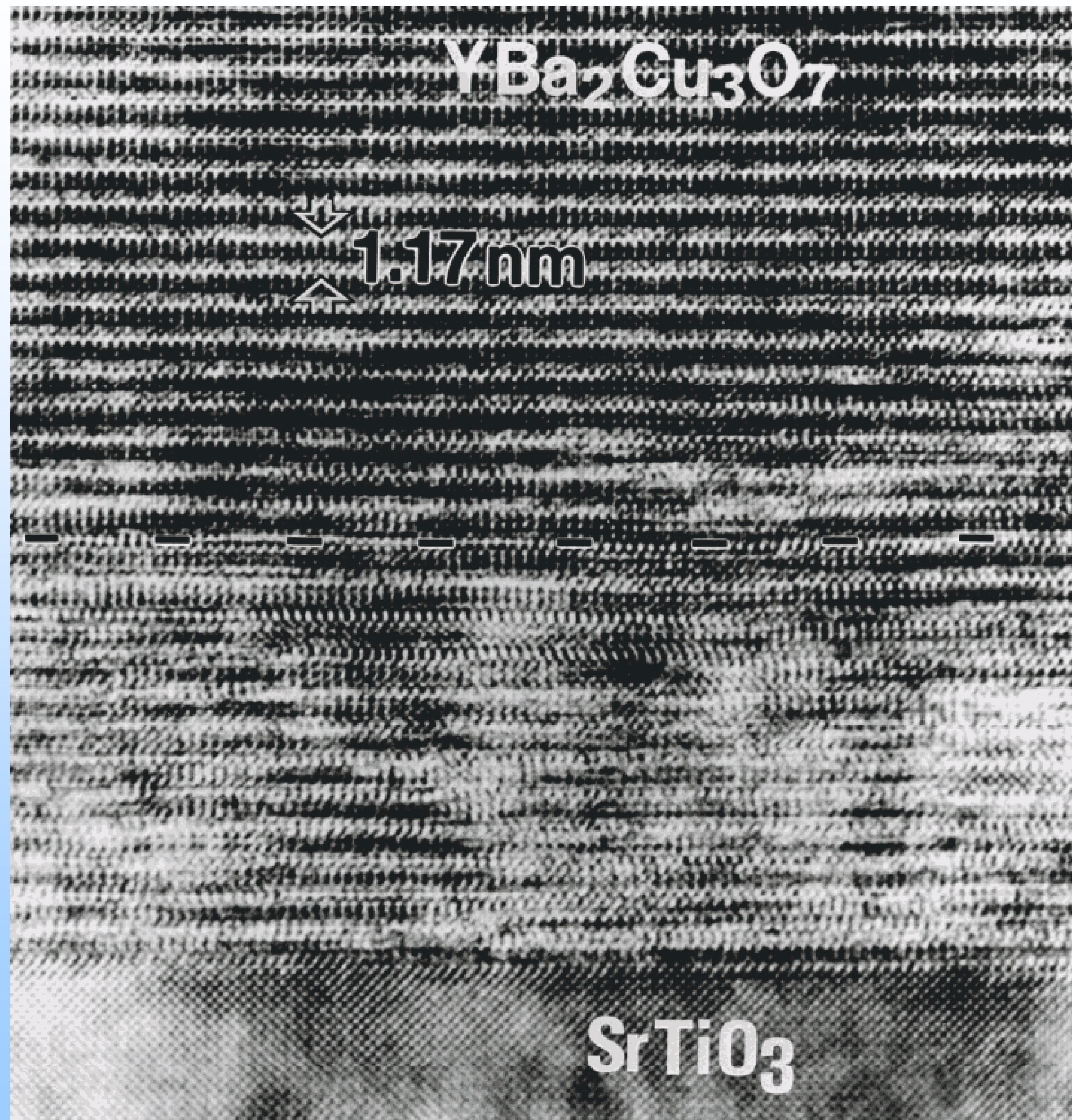
- Preparation of various materials

Disadvantages

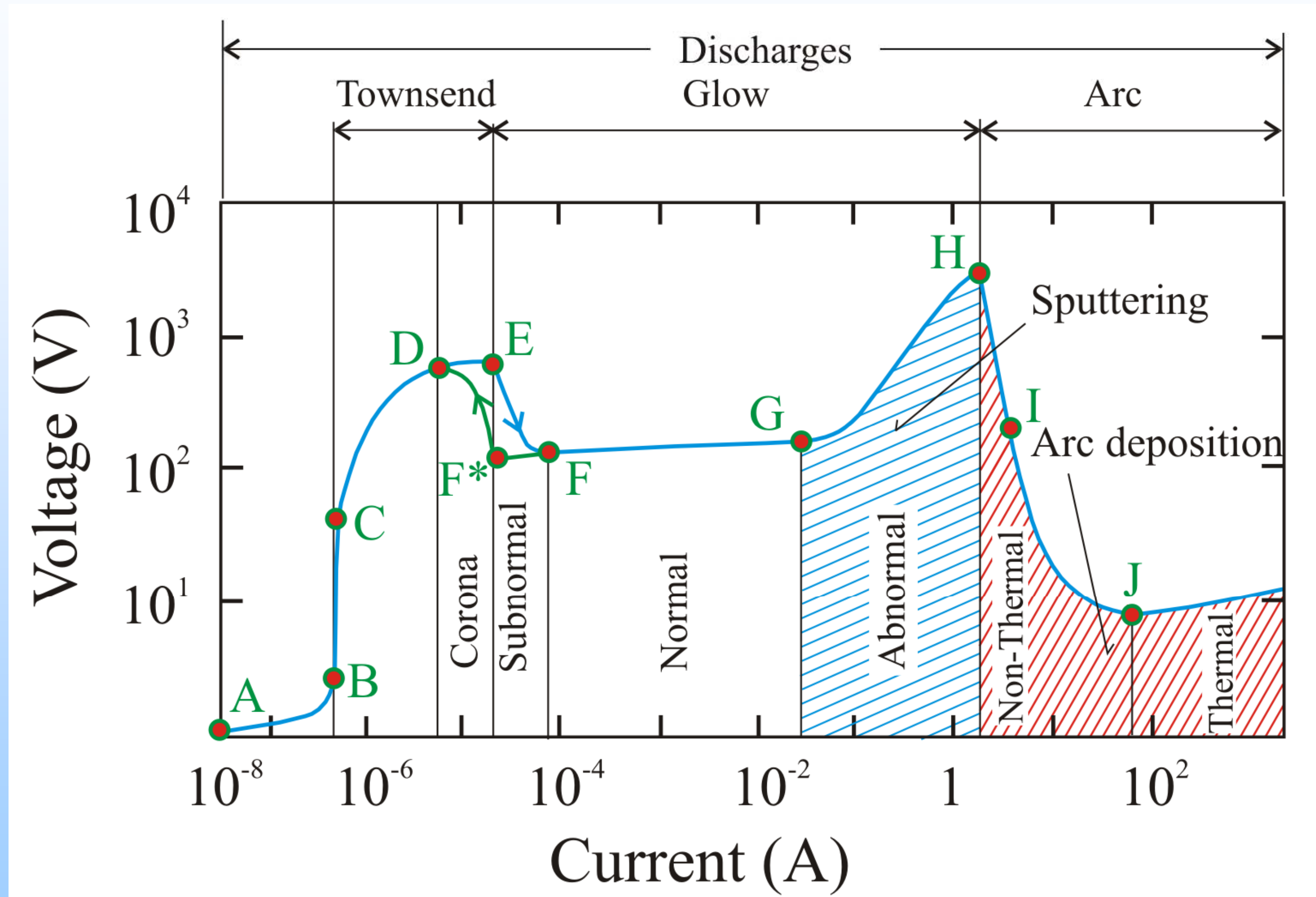
- Droplet formation - can be suppressed
- Limitation in large area deposition
- High cost of excimer lasers

Importance

- Deposition of novel materials and devices
- Research in laboratories
- Small-scale production of high cost performance devices
- In near future an improved pulsed laser with low cost will be available, leading to mass production

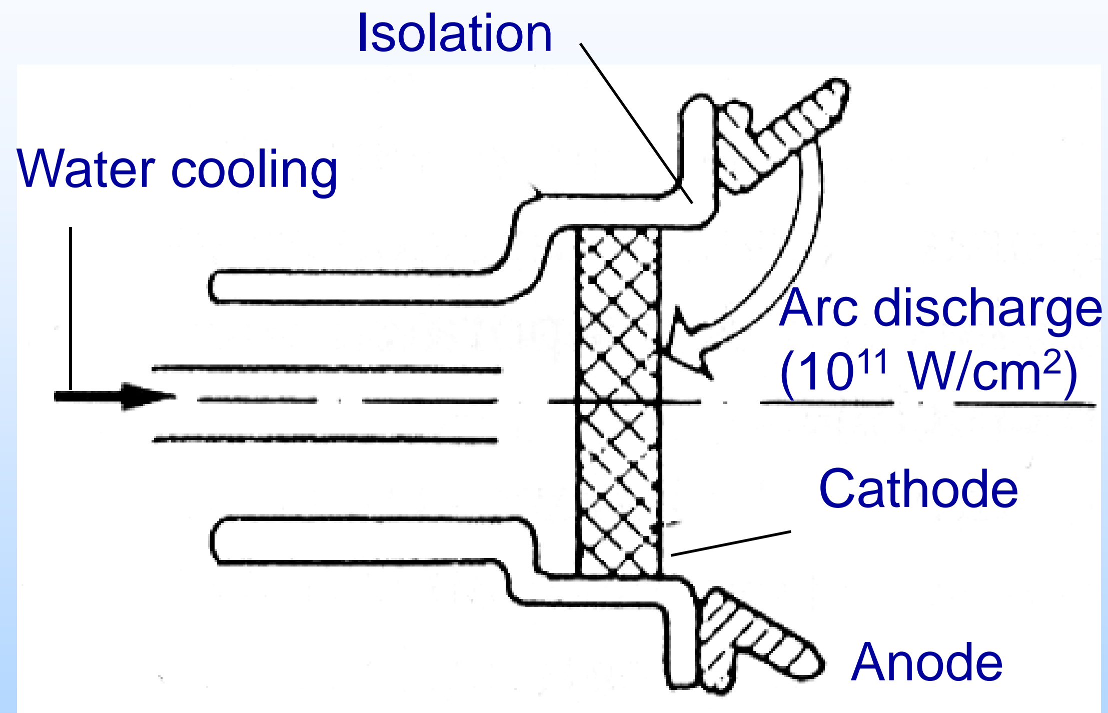

$YBa_2Cu_3O_7$
1.17 nm
$SrTiO_3$

Cathodic Vacuum Arc



I-V characteristic showing the regimes of discharges

Arc-Evaporation



Arc

- Self- sustaining
- Hot spots on cathode
- I > 1 A

Vacuum arc can sustain without any gas

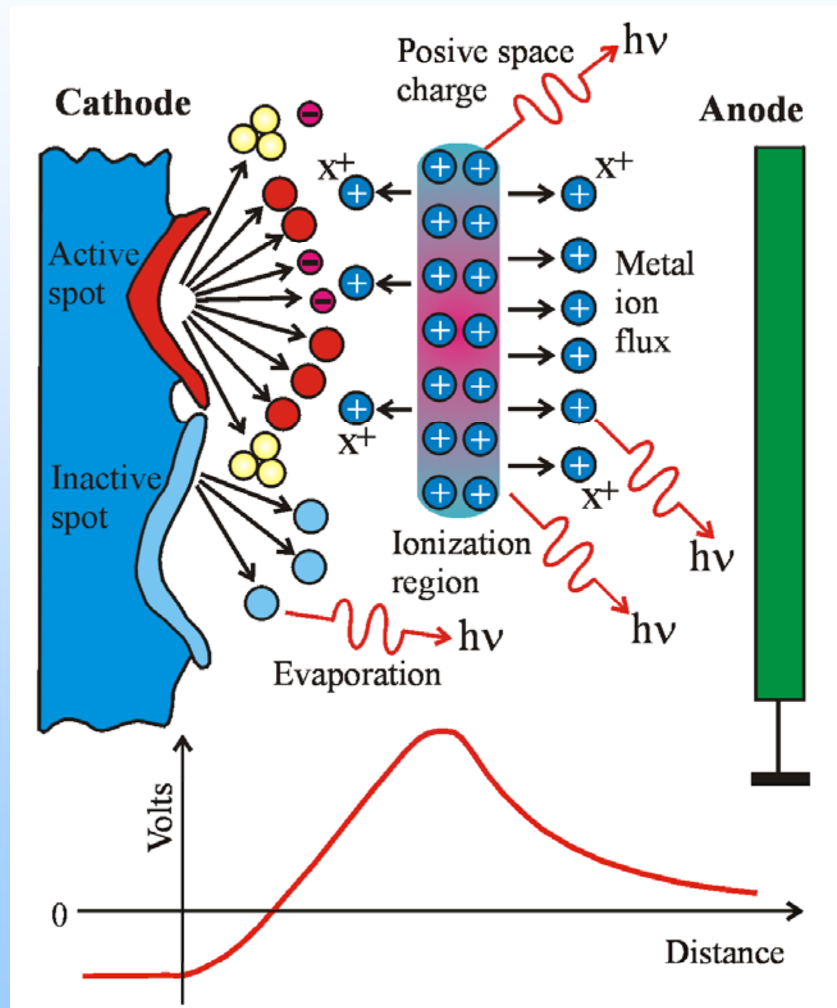
- When triggered - feedback mechanism is established.
- Secondary and thermionic emission
- Cathode material is fed into discharge from hot spots

Droplets – evaporation

→ Film composition = Cathode composition

→ Advantage for compounds and alloys

Cathode Processes



Cathode feeds

- Electrons
- Electrode Vapors (Ions, neutrals)
- Active and inactive spot evaporation
- Macroparticles
- Photons from hot spots

Ionization region

- Electron impact, positive ions, photons
- Positive space charge - potential hump (near hot spot)
  - Resulting in ion **KE (20 - 100 eV)** > energy corresponding to the arc voltage **(10-30 V)**
  - Neutrals **5 eV**

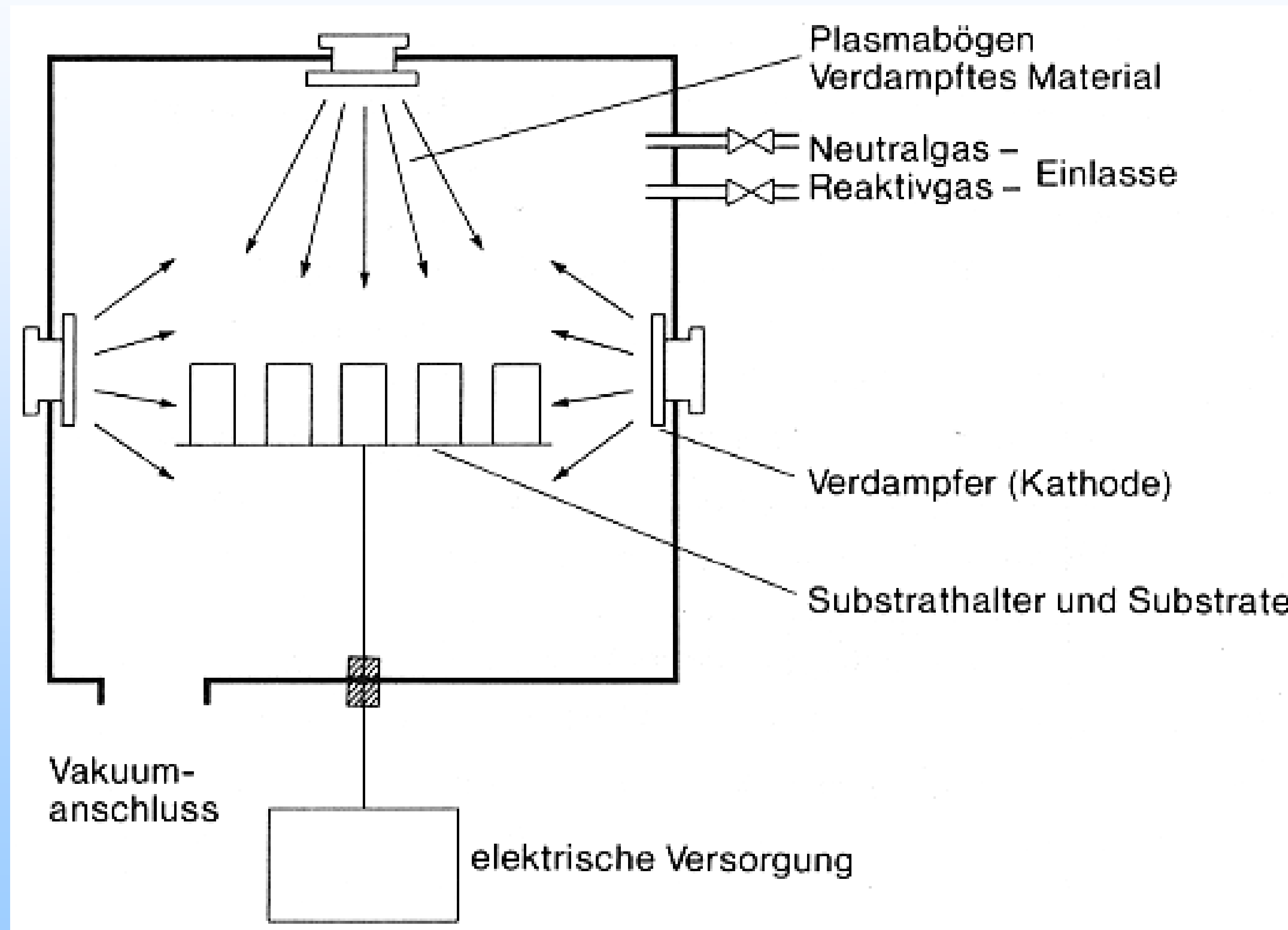
Fundamental Properties of Vacuum Arc Plasma

- Few neutral species
- High KE ions: 20 – 100 eV > arc voltage
- E field is week
- Current “I” carried by ions is 8%
- Current density 10^2 – 10^8 A/cm^2
- Intense nearly isothermal plasma

Arc with Respect to the Cathode

- Hot cathode spot ~ 10^{-8} – 10^{-4} m
- Hot spot moves over the cathode
- Speed of moving hot spot depends on the cathode material and presence of mg. field.
- Erosion depends on the cathode spot and surface state - change with cleaning of the cathode from oxide and other contaminants

3D Possibility of Arc - Evaporation



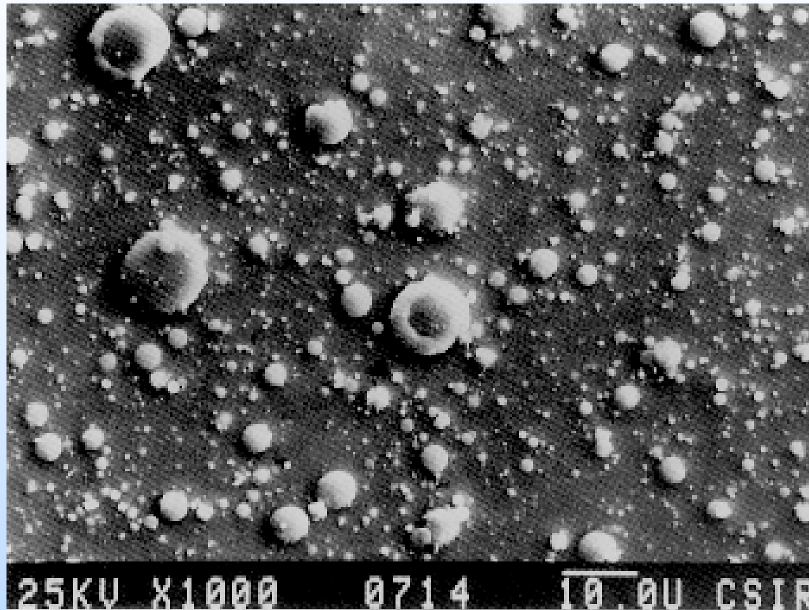
Ion Emission

- Mostly emitted ionized material
- Macro-droplets
- KE of ions emitted from cathode spots > cathode-anode voltage
  - (a) Because of the formation of potential hump
  - (b) Multiple charged ions: Ions with Z = 6 detected
- Fractional ionization for Ti: 0.7 under high vacuum; and 0.85 at N pressure 0.1 - 1.5 Pa

Electron Emission

- Energy 3 – 6 eV for Cu; 6 – 9 eV for Al
- Density 1 – 5×10^{14} cm^{-3}

Macroparticles Emission

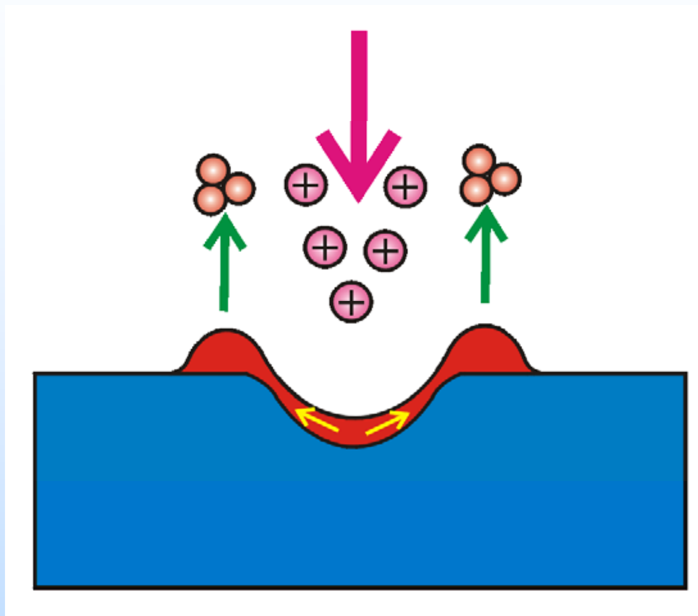


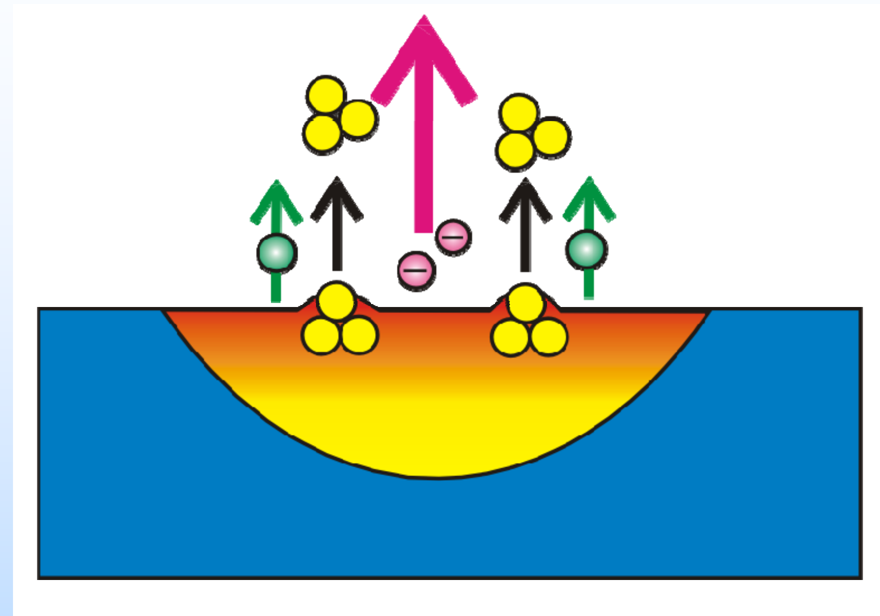
SEM micrograph of macroparticles on Ti metal deposited by cathodic arc.

- Size: ~ 0.1 - 2 μm
- Emitted at small angles ~ 20º
- Velocity 0.1 – 800 m/s
- Their emission and the erosion rate of cathode decreases with the increase in melting point of cathode materials

Cu: 25 – 26 μg/As;
Cd: 245 – 360 μg/As
W: less than 1% macroparticles

Macroparticles Emission - Models





(a) Ions accelerated towards liquid surface of hot spot → vapor jet recoil forces presses inward on the molten metal and material is pushed towards edge of crater yielding the observed distribution.

(b) Explosive emission: Electrons are concentrated on small protrusion on the cathode → rapid heating by e^{-}s until explosions. (Rapid evaporation - higher temperature below surface)

$p = 2 \times 10^{10}$ Pa

Macroparticle Suppression - Elimination

- Reducing the cathode temperature by cooling
- Low arc current
- Suitable placement of substrate with respect to the cathode plane
- Presence of oxides or nitrides on the surface cathode reduces macroparticles
- Construction of macroparticle filters.