# Vékonyrétegek előállítása és alkalmazásai

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# Classification

EVAPORATIVE METHODS

• *Vacuum Evaporation*

Conventional vacuum evaporation

Electron-beam evaporation

Molecular-beam epitaxy (MBE)

Reactive evaporation

GLOW-DISCHARGE PROCESSES

• *Sputtering*

Diode sputtering
Reactive sputtering
Bias sputtering (ion plating)
Magnetron sputtering
Ion beam deposition
Ion beam sputter deposition
Reactive ion plating
Cluster beam deposition (CBD)

• *Plasma Processes*

Plasma-enhanced CVD
Plasma oxidation
Plasma anodization
Plasma polymerization
Plasma nitridation
Plasma reduction
Microwave ECR plasma CVD
Cathodic arc deposition

GAS-PHASE CHEMICAL PROCESSES

• *Chemical Vapor Deposition (CVD)*

CVD epitaxy
Atmospheric-pressure CVD (APCVD)
Low-pressure CVD (LPCVD)
Metalorgainc CVD (MOCVD)
Photo-enhanced CVD (PHCVD)
Laser-induced CVD ((LCVD)
Electron-enhanced CVD

• *Thermal Forming Processes*

Thermal oxidation
Thermal nitridation
Thermal polymerization

Ion implantation

LIQUID-PHASE CHEMICAL TECHNIQUES

• *Electro Processes*

Electroplating
Electroless plating
Electrolytic anodization
Chemical reduction plating
Chemical displacement plating
Electrophoretic deposition

• *Mechanical Techniques*

Spary pyrolysis
Spray-on techniques
Spin-on techniques

Liquid phase epitaxy

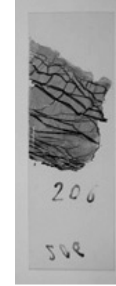
Krishna Seshan: HANDBOOK OF THIN-FILM DEPOSITION PROCESSES AND TECHNIQUES
Principles, Methods, Equipment and Applications, 2nd ed., 2002 by Noyes Publications

# Evaporation

The objective of this deposition process is to controllably transfer atoms from a ***heated*** source to a substrate. Thermal energy is imparted to atoms in a liquid or solid source such that their temperature is raised to a point where they either efficiently evaporate or sublime.

Earliest attempts dates back to 1857 when Faraday made thin films via exploding wires in an inert atmosphere.

Some of the boxes containing Faraday's slide specimens.



One of Faraday's gold films (#206).

Evaporation was the preferred Physical Vapor Deposition technique for growing thin films until the late 1960s. Higher deposition rates, better vacuum and cleaner environments were and still are the major advantages of this technique.

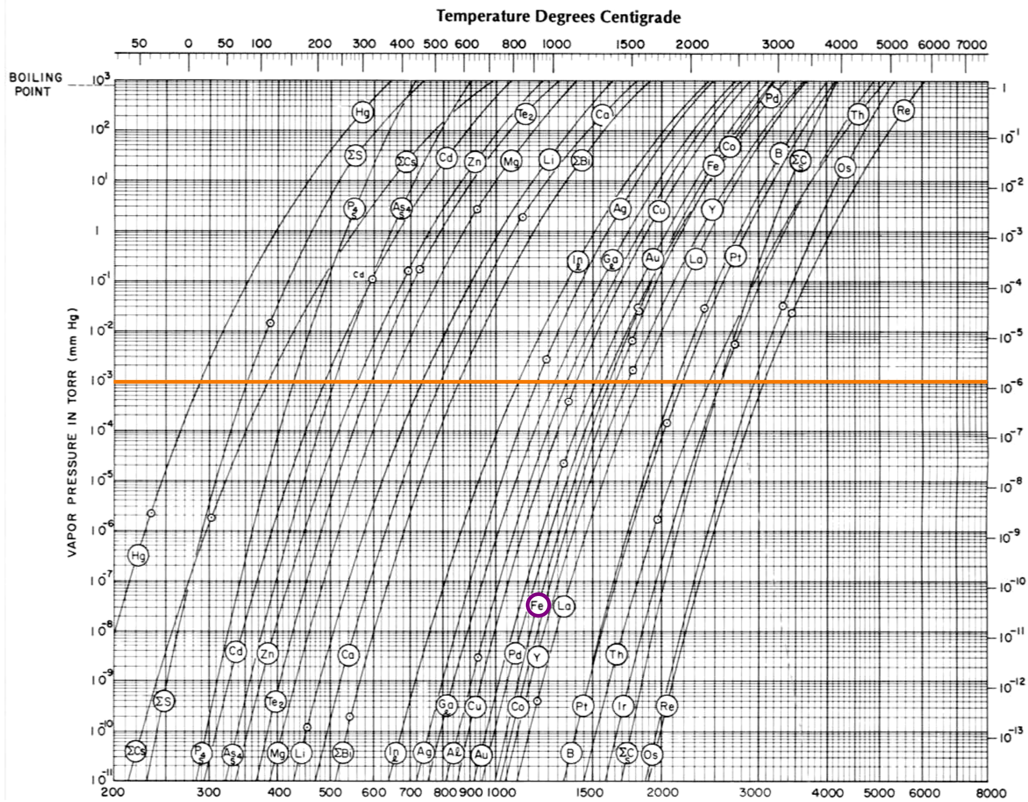
# Rate of evaporation

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

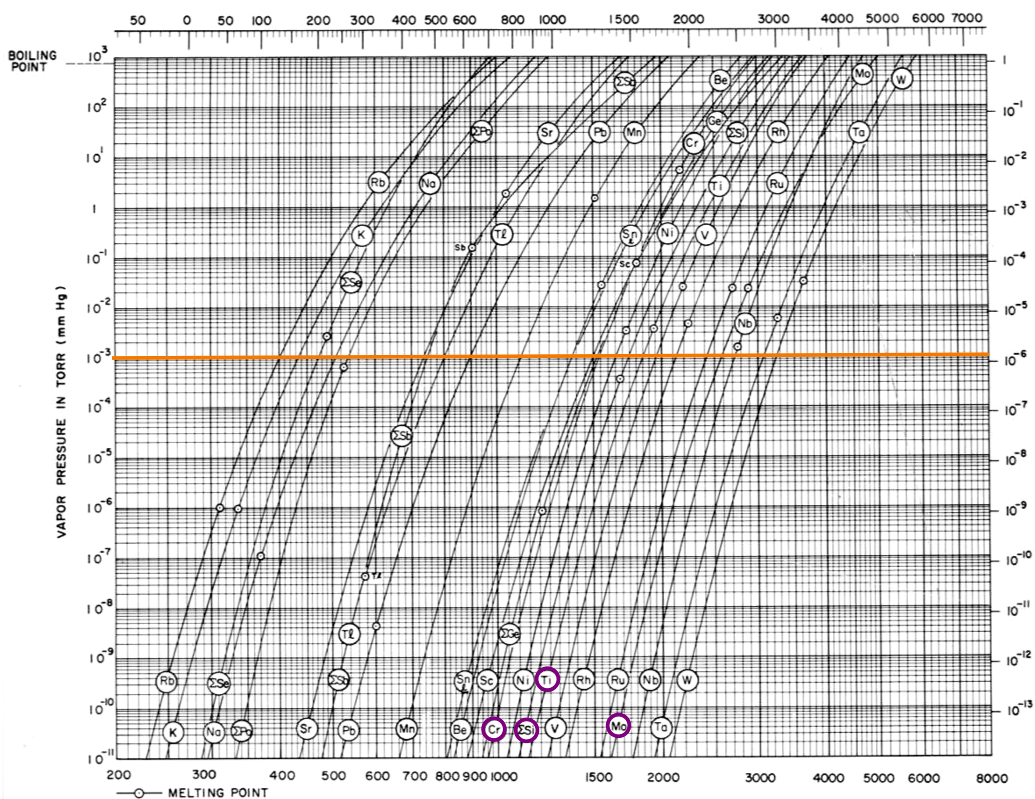
$\Phi_e$: evaporation flux (number of species evaporated per unit time and unit area)
$\alpha_e$: coefficient of evaporation (0-1)
$P_e$: equilibrium/saturated vapor pressure
$P_h$: hydrostatic pressure acting on the evaporant
$M$: molecular weight
$T$: absolute temperature
$N_A$: Avogadro's number
$R$: universal gas constant

The key variable influencing evaporation rate is the temperature via $P_e(T)$.

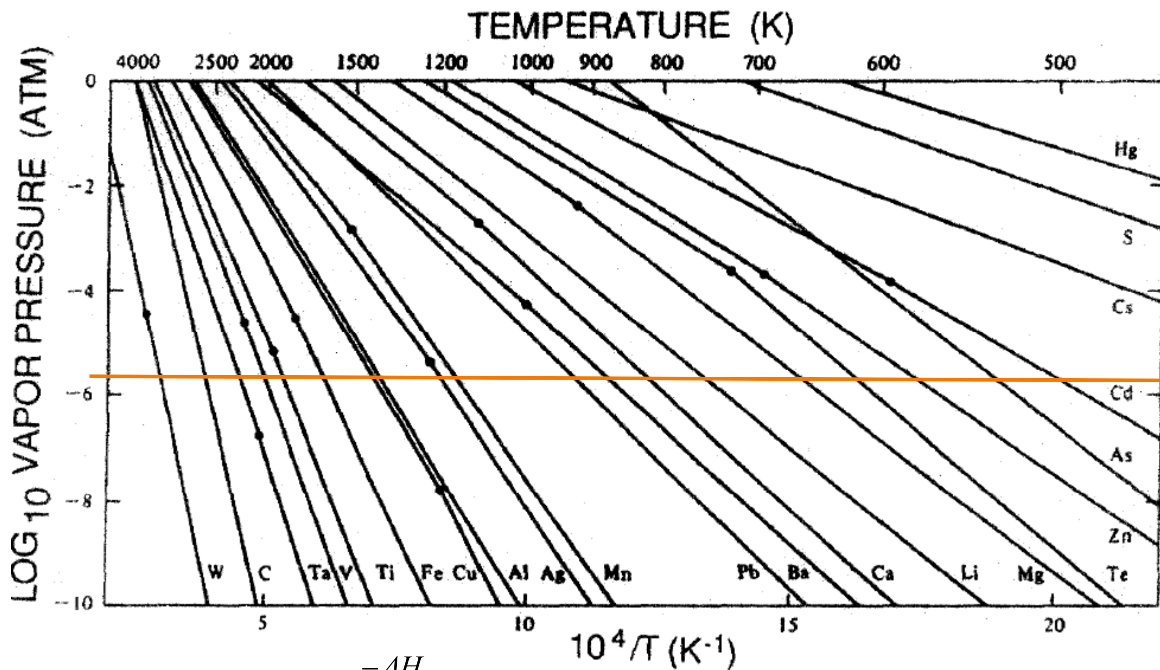
# Temperature dependence of the vapor pressure of selected elements 1.




# Temperature dependence of the vapor pressure of selected elements 2.



# Temperature dependence of the vapor pressure of selected elements 3.




$$p = p_0 e^{\frac{-\Delta H_e}{RT}}$$

$\Delta H_e$: molar heat of evaporation

Rule of thumb: melt will be required if the element does not achieve a vapor pressure greater than $10^{-3}$ torr at its melting point. e.g. Cr, Ti, Mo, Fe or Si

# Evaporation of multielement materials

Whereas metals essentially evaporate as atoms (or maybe clusters of atoms) the same is not true of compounds. Very few inorganic compounds evaporate without molecular change → the vapour composition is different from that of the original solid or liquid source → the stoichiometry of the deposit will differ from that of the source.

The elements of alloys also evaporate preferentially. The composition is hard to keep.

**Disadvantage of the technique**

| Reaction type | Chemical reaction[a] | Examples | Comments |
|---|---|---|---|
| Evaporation without dissociation | $MX(s \text{ or } l) \rightarrow MX(g)$ | $SiO$, $B_2O_3$, $GeO$, $SnO$, $AlN$, $CaF_2$, $MgF_2$ | Compound stoichiometry maintained in deposit |
| Decomposition | $MX(s) \rightarrow M(s) + \frac{1}{2}X_2(g)$<br>$MX(s) \rightarrow M(l) + \frac{1}{n}X_n(g)$ | $Ag_2S$, $Ag_2Se$<br>III–V semiconductors | Separate sources are required to deposit these compounds |
| Evaporation with dissociation | | | Deposits are metal-rich |
| (a) Chalcogenides | $MX(s) \rightarrow M(g) + \frac{1}{2}X_2(g)$<br>X = S, Se, Te | CdS, CdSe, CdTe | Separate sources usually required to deposit these compounds |
| (b) Oxides | $MO_2(s) \rightarrow MO(g) + \frac{1}{2}O_2(g)$ | $SiO_2$, $GeO_2$, $TiO_2$, $SnO_2$, $ZrO_2$ | Metal-rich discolored deposits; dioxides are best deposited in $O_2$ partial pressure (reactive evaporation) |

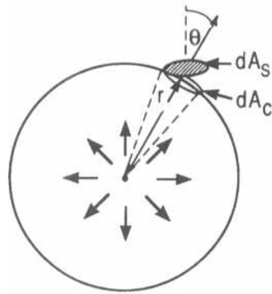
[a] M = metal, X = nonmetal.

Maintaining stoichiometry may be achieved by:

0) sufficiently large volume of melt
1) evaporation from two or more independent elemental sources
2) continuously adjusting the composition of a single source

# Deposition geometry 1.

**Point source**




$$dA_c = dA_s \cos\theta$$ the effective (projected) area of the substrate

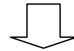
$M_e$: the total evaporated mass (leaving the source)

$dM_s$: portion of evaporated material landing on the substrate

$$dM_s : M_e = dA_c : 4r^2\pi$$

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

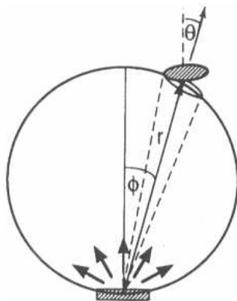
if we refer the mass to unit time the left hand side gives the deposition rate of the material.



Substrates placed in a way that their surface normal is radial are coated uniformly.

# Deposition geometry 2.

**Surface source**




$\phi$: emission angle of evaporant

$\theta$: deposition or receiving angle

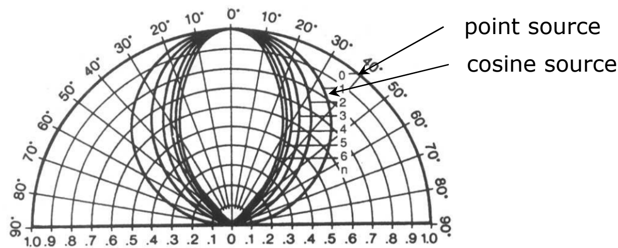
The extended source is a superposition of many point sources.

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

Knudsen cell, or effusion cells (c.f. MBE)

# Deposition geometry 3.

**A more realistic, $\cos^n\phi$ surface source**




In many cases a $\cos^n\phi$ evaporation law is more realistic:

$$\frac{d\dot{M}_s}{dA_s} = \frac{M_e(n+1)\cos^n\phi\cos\theta}{2\pi r^2} \qquad n \geq 1$$

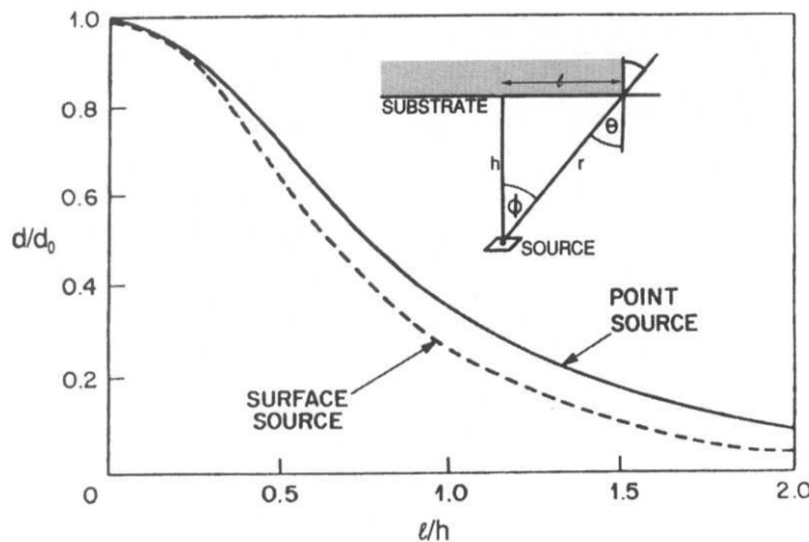
*n*: a number that determines the geometry of the vapor cloud, i.e. n is related to the evaporation crucible geometry and scales with the ratio of the melt depth to the melt surface.

Deep and narrow crucibles have large *n* that confine the evaporated material (e.g. can be used to minimize radioactive waste and chamber contamination).

As the source become more and more directional the receiving surface area, effectively exposed to the evaporant, shrinks.

$$4r^2\pi \;\rightarrow\; r^2\pi \;\rightarrow\; \frac{2r^2\pi}{n+1}$$

# Thickness distribution




Point source:

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

$$d_0 = M_e / 4\pi\rho h^2$$

Surface source:

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

$$d_0 = M_e / \pi\rho h^2$$

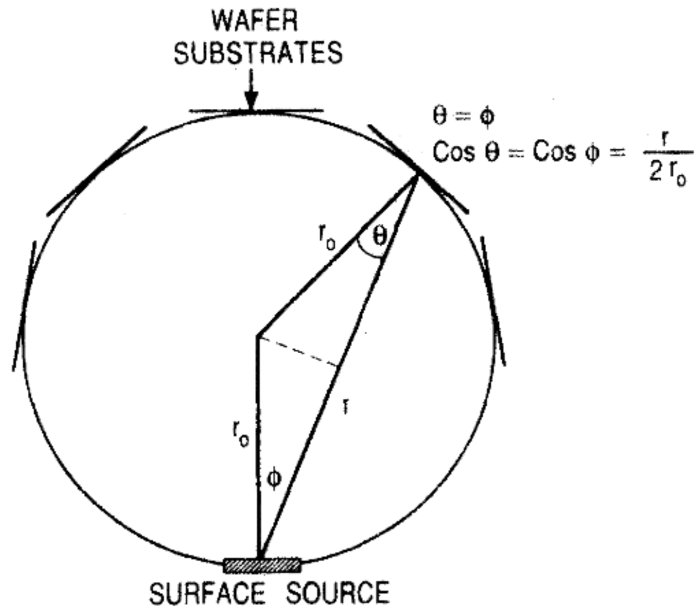
It is evident that a point source will achieve more uniform thickness distribution. Actually, thickness uniformity is critically dependent upon source-substrate geometry. Can be affected by varying the location of source and substrate and using static and rotating shutters. Maintaining thickness uniformity is always desirable, but not necessarily required. Yet it is absolutely essential for microelectronic and optical coating applications.

# Thickness uniformity

A clever way to achieve uniform thickness is to place the source and the substrates on the surface of a sphere.

In this geometry

$$\frac{dM_s}{dA_s} = \frac{M_e \cos\phi \cos\theta}{\pi r^2} = \frac{M_e}{\pi r^2} \frac{r}{2r_0} \frac{r}{2r_0} = \frac{M_e}{4\pi r_0^2}$$




Clearly independent of angle, since
- short source-substrate distances are offset by unfavourably large vapor emission and deposition angles, while
- long source-substrate distances are compensated by correspondingly small emission and reception angles.

The columnar grain structure is NOT preserved.

# Film purity

Purity of the evaporated films depends on the level of impurities present in
- the source material
- heater, crucible or support materials
- gas(es) present in the vacuum chamber

During deposition the species of both the evaporant and the residual gases impinge on the substrate in parallel, independent events.

**Evaporant**

$$\Phi_e = \frac{\rho \cdot N_A \cdot \dot{d}}{M_e}$$

$\Phi_e$: impingment rate of evaporant vapour
$\rho$: density of evaportant
$N_A$: Avogadro's number
$d$: deposition rate
$M_e$: molecular weight of evaporant

**Residual gas**

$$\Phi_{rg} = \frac{P \cdot N_A}{\sqrt{2\pi M_{rg} RT}}$$

$\Phi_{rg}$: impingment rate of residual gas
$P$: pressure of residual gas
$N_A$: Avogadro's number
$M_{rg}$: molecular weight of residual gas
$R$: universal gas constant
$T$: absolute temperature

$$C_i = \frac{\Phi_{rg}}{\Phi_e} = \frac{P \cdot N_A}{\sqrt{2\pi M_{rg} RT}} \Bigg/ \frac{\rho \cdot N_A \cdot \dot{d}}{M_e} = \frac{P \cdot M_e}{\rho \cdot \dot{d} \sqrt{2\pi M_{rg} RT}} \propto \frac{P \cdot M_e}{\rho \, \dot{d} \sqrt{M_{rg} T}}$$

$C_i$: impurity concentration

# Film purity, cont.

| $P_{O_2}$ (torr) | Deposition rate (Å/s) 1 | 10 | 100 | 1000 |
|---|---|---|---|---|
| $10^{-9}$ | $10^{-3}$ | $10^{-4}$ | $10^{-5}$ | $10^{-6}$ |
| $10^{-7}$ | $10^{-1}$ | $10^{-2}$ | $10^{-3}$ | $10^{-4}$ |
| $10^{-5}$ | 10 | 1 | $10^{-1}$ | $10^{-2}$ |
| $10^{-3}$ | $10^{3}$ | $10^{2}$ | 10 | 1 |

max. $O_2$ concentration in Sn films deposited at room temperature

Ref: H.L. Caswell, in *Physics of Thin Films*, Vol. 1 G. Hass, ed. Academic Press, NY, 1963

In order to produce very pure films, it is important to deposit at very high rates while maintaining very low background pressures of residual gases.

This is not a stringent requirement for evaporation since deposition rates can reach 1000Å/s at chamber pressures of $10^{-8}$ torr (e.g. via electron beam evaporation).

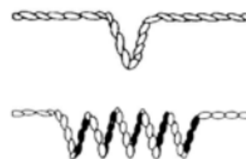
(As opposed to this, maintaining low impurity levels is much harder in sputtering, where typical deposition rates are two orders of magnitude smaller and chamber pressures are four orders of magnitude larger.)

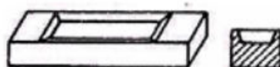
# Electrically heated evaporation sources

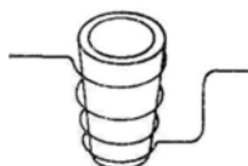
Material of the crucible must have negligible vapour pressure at the evaporation temperature AND remain chemically inert.

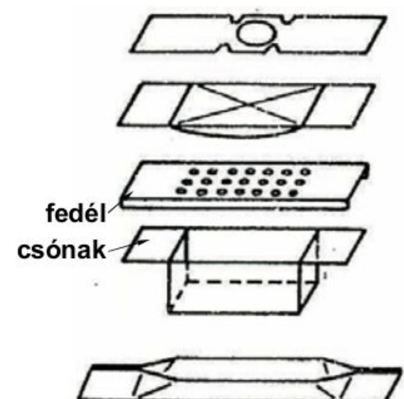
Type of evaporation sources:

- Tungsten wire (wetting, $T_e$<2200°C)
- Refractory metal (W, Ta, Mo) boats, strips
- Sublimation furnace (for S, Se and oxides)
- Crucibles: cylindrical cups, made of oxides, BN, graphite, refractory metals (direct, resistive or inductive heating)









# Evaporation characteristics of materials

| Material | Minimum evaporation temperature[a] | State of evaporation | Recommended crucible material | Deposition rate (Å/s) | Power (kW) (e-beam[b]) |
|---|---|---|---|---|---|
| Aluminum | 1010 | Melts | BN | 20 | 5 |
| $Al_2O_3$ | 1325 | Semimelts | | 10 | 0.5 |
| Antimony | 425 | Melts | BN, $Al_2O_3$ | 50 | 0.5 |
| Arsenic | 210 | Sublimes | $Al_2O_3$ | 100 | 0.1 |
| Beryllium | 1000 | Melts | Graphite, BeO | 100 | 1.5 |
| BeO | | Melts | | 40 | 1.0 |
| Boron | 1800 | Melts | Graphite, WC | 10 | 1.5 |
| BC | | Semimelts | | 35 | 1.0 |
| Cadmium | 180 | Melts | $Al_2O_3$, quartz | 30 | 0.3 |
| CdS | 250 | Sublimes | Graphite | 10 | 0.2 |
| $CaF_2$ | | Semimelts | | 30 | 0.05 |
| Carbon | 2140 | Sublimes | | 30 | 1.0 |
| Chromium | 1157 | Sublimes | W | 15 | 0.3 |
| Cobalt | 1200 | Melts | $Al_2O_3$, BeO | 20 | 2.0 |
| Copper | 1017 | Melts | Graphite, $Al_2O_3$ | 50 | 0.2 |
| Gallium | 907 | Melts | $Al_2O_3$, graphite | | |
| Germanium | 1167 | Melts | Graphite | 25 | 3.0 |
| Gold | 1132 | Melts | $Al_2O_3$, BN | 30 | 6.0 |
| Indium | 742 | Melts | $Al_2O_3$ | 100 | 0.1 |
| Iron | 1180 | Melts | $Al_2O_3$, BeO | 50 | 2.5 |
| Lead | 497 | Melts | $Al_2O_3$ | 30 | 0.1 |
| LiF | 1180 | Melts | Mo, W | 10 | 0.15 |
| Magnesium | 327 | Sublimes | Graphite | 100 | 0.04 |
| $MgF_2$ | 1540 | Semimelts | $Al_2O_3$ | 30 | 0.01 |
| Molybdenum | 2117 | Melts | | 40 | 4.0 |
| Nickel | 1262 | Melts | $Al_2O_3$ | 25 | 2.0 |
| Permalloy | 1300 | Melts | $Al_2O_3$ | 30 | 2.0 |
| Platinum | 1747 | Melts | Graphite | 20 | 4.0 |
| Silicon | 1337 | Melts | BeO | 15 | 0.15 |
| $SiO_2$ | 850 | Semimelts | Ta | 20 | 0.7 |
| SiO | 600 | Sublimes | Ta | 20 | 0.1 |
| Tantalum | 2590 | Semimelts | | 100 | 5.0 |
| Tin | 997 | Melts | $Al_2O_3$, graphite | 10 | 2.0 |
| Titanium | 1453 | Melts | | 20 | 1.5 |
| $TiO_2$ | 1300 | Melts | W | 10 | 1.0 |
| Tungsten | 2757 | Melts | | 20 | 5.5 |
| Zinc | 250 | Sublimes | $Al_2O_3$ | 50 | 0.25 |
| ZnSe | 660 | Sublimes | Quartz | | |
| ZnS | 300 | Sublimes | Mo | | |
| Zirconium | 1987 | Melts | W | 20 | 5.0 |

[a] Temperature (°C) at which vapor pressure is $10^{-4}$ torr.
[b] For 10 kV, copper herth, source–substrate distance of 40 cm.

# Evaporation Support Materials

Refractory metals:
- Tungsten (W); MP = 3380°C, P* = $10^{-2}$ torr at 3230°C
- Tantalum (Ta); MP = 3000°C, P* = $10^{-2}$ torr at 3060°C
- Molybdenum (Mo); MP = 2620°C, P* = $10^{-2}$ torr at 2530°C

Refractory ceramics:
- Graphitic Carbon (C); MP = 3700°C, P* = $10^{-2}$ torr at 2600°C
- Alumina (Al2O3); MP = 2030°C, P* = $10^{-2}$ torr at 1900°C
- Boron nitride (BN); MP = 2500°C, P* = $10^{-2}$ torr at 1600°C

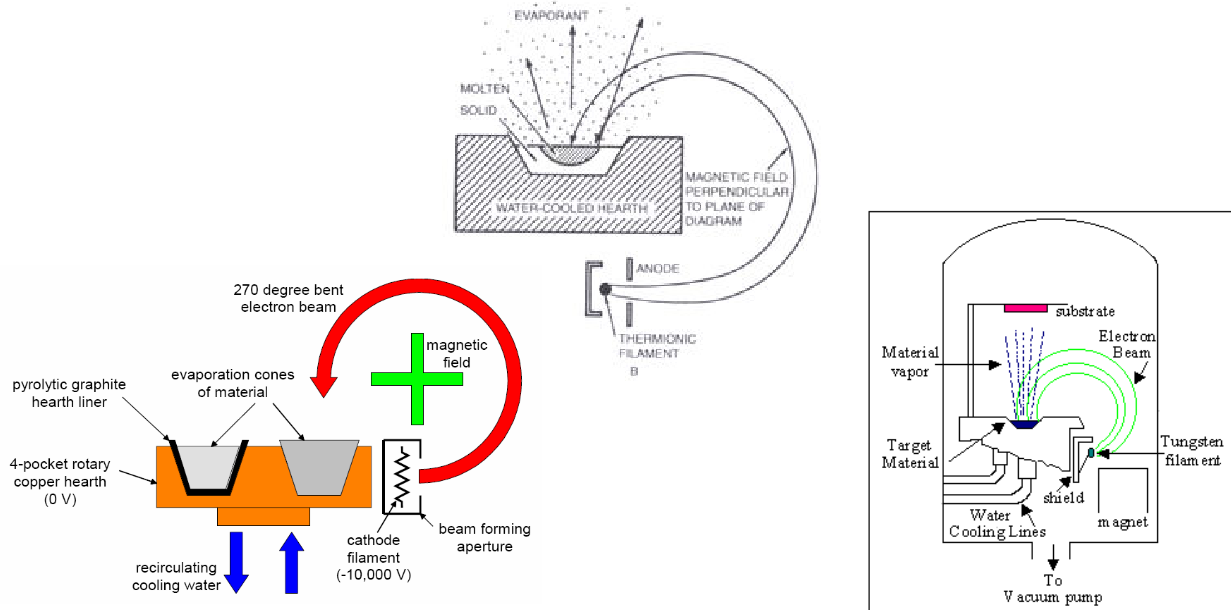
Engineering considerations:
- Thermal conductivity
- Thermal expansion
- Electrical conductivity
- Wettability and reactivity

# Electron beam evaporation

Most popular method.

Localised heating -> smaller contamination

E-gun: thermionic emission from heated filaments, magnetic deflection to avoid contamination.




## Resistance Heated Evaporation

- Simple, robust, and in widespread use.
- Can only achieve temperatures of about 1800°C.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Typical deposition rates are 1-20 Angstroms/second.
- Common evaporant materials:
  - Au, Ag, Al, Sn, Cr, Sb, Ge, In, Mg, Ga
  - CdS, PbS, CdSe, NaCl, KCl, AgCl, $MgF_2$, $CaF_2$, $PbCl_2$

## Electron Beam Heated Evaporation

- More complex, but extremely versatile.
- Can achieve temperatures in excess of 3000°C.
- Use evaporation cones or crucibles in a copper hearth.
- Typical emission voltage is 8-10 kV.
- Exposes substrates to secondary electron radiation.

– X-rays can also be generated by high voltage electron beam.

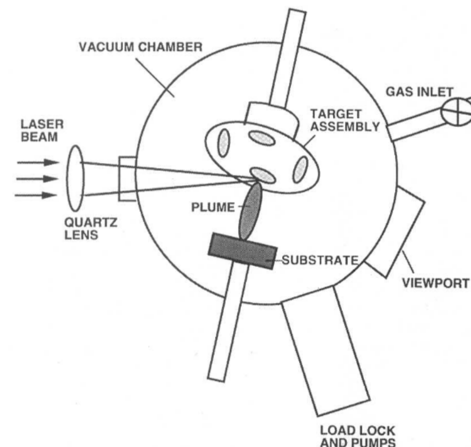
- Typical deposition rates are 10-100 Angstroms/second.
- Common evaporant materials:
  - Everything a resistance heated evaporator will accommodate, plus:
  - Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo
  - $Al_2O_3$, SiO, $SiO_2$, $SnO_2$, $TiO_2$, $ZrO_2$

# Pulsed Laser Deposition (PLD)

Utilizes a laser pulse for the flash evaporation of the target materials and subsequent film growth.

Most typical laser sources:

- excimers (ArF 193nm; KrF 248nm or XeCl 308nm)
- Nd:YAG lasers at the fundamental (1064nm) or its frequency multipled wavelengths (532nm, 355nm or 266nm)



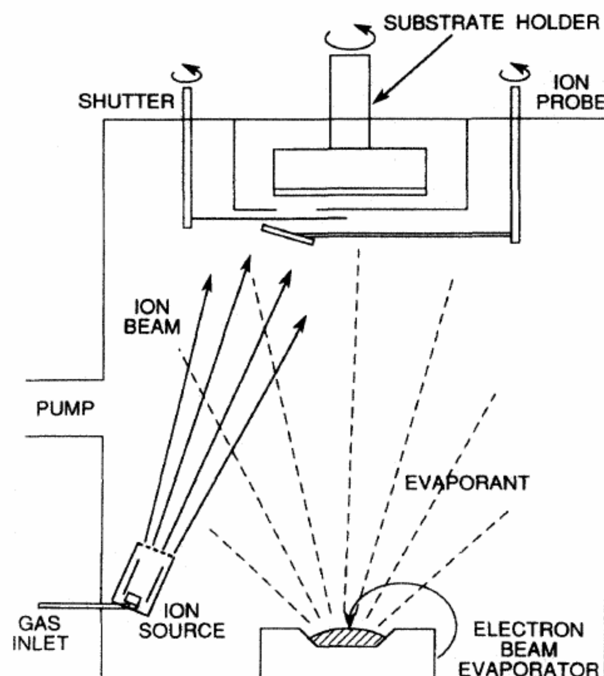

**Benefits:**

- Almost all materials can be deposited, even ceramics which are usually difficult to evaporate.
- Crystallinity, composition can be tuned.
- Fine control of thickness (growth of sub-ML per laser pulse).
- Can keep stoichiometry under proper conditions.

**Disadvantages:**

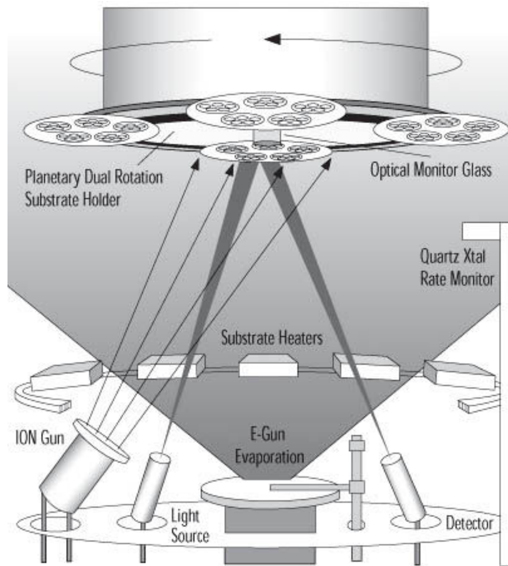
- Highly directional plume → $8 < n < 12$ → non-uniform thinkness distribution.
- Energetic particulates (clusters, solid or molten particles) deteriorate the film uniformity
- Growth of large area film requires sophisticated apparatus for target/substrate movement.

# Ion Beam Assisted Deposition




The energetic ions assist in the densification of the growing layer.

# BROADBAND ANTI-REFLECTION (BBAR) coating




**Steps:**
1) Prepare tooling to mount optics in chamber.
2) Clean optics and load them into tooling.
3) Clean chamber and refill with source material needed to produce coating evaporates. Prepare monitoring system.
4) Load tooling containing optical components into chamber.
5) Reduce chamber pressure to <2 x 10-5 Torr and heat chamber to 200 - 300°C.
6) Deposit coating layers as per coating design.
7) Cool and vent coating chamber.
8) Remove optics from chamber and test optics for coating performance.
9) Inspect and wrap optics.
Total Cycle time for BBAR is over 3 hrs not including cleaning and inspection.

www.zcrcoatings.com