F4280 Technology of Thin Film Deposition & Surface Treatments
3. Evaporation

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3.1 Introduction to Evaporation

Vacuum (high temperature) evaporation as the method of thin film deposition is purely physical process (belongs to physical vapor deposition methods - PVD). It is composed of three subsequent steps:

1. Obtaining the vapors of solid materials that do not have high enough vapor pressure (vaporization) $\Rightarrow$ materials are heated to so high temperatures that they melt and evaporate at sufficiently high vapor pressure.
2. Transport of vapors from the source to the substrate.
3. Condensation of vapors in the form of thin film on much colder substrate.

Some historical facts:

- In 1857, Faraday created thin metallic films by exploding metal wires in a vacuum.
- Although sputtering and sputter-deposition were reported in the mid-1800s using oil seed piston pumps, vacuum evaporation had to await better vacuum provided by the Springer mercury-column vacuum pumps. In 1879, Edison used this type of pump to evacuate the first carbon-filament incandescent lamp (and observed deposition of carbon thin film).
- In 1887, Nahrwold performed the first thermal vacuum evaporation (from crucible).
- Vacuum evaporation of metallic thin films was not common until 1920s.

https://www.svc.org/HistoryofVacuumCoating/History-of-Vacuum-Coating.cfm

3.1 Physical Vapor Deposition (PVD) Techniques

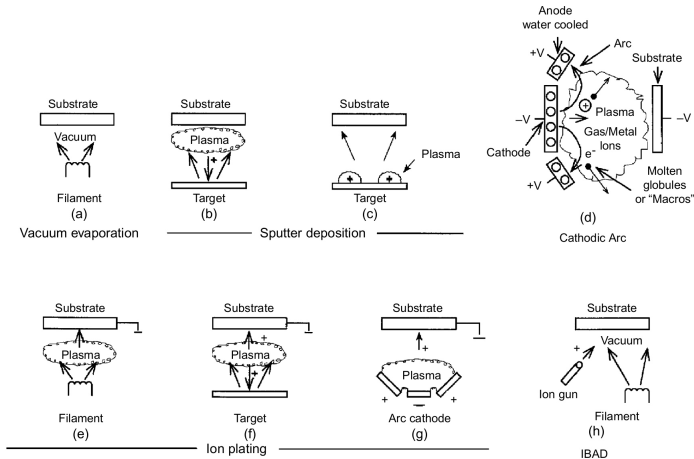


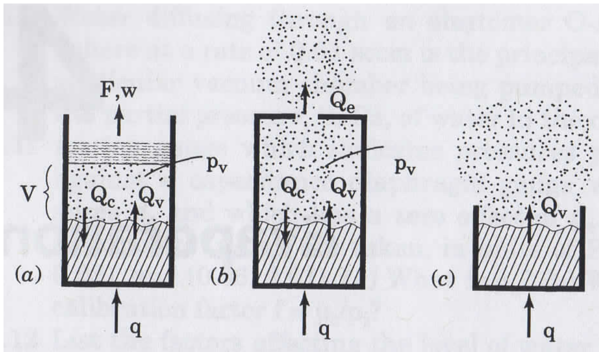
Figure 1.1: PVD Processing Techniques: (a) Vacuum Evaporation, (b) and (c) Sputter Deposition in a Plasma Environment, (d) Sputter Deposition in a Vacuum, (e) Ion Plating in a Plasma Environment with a Thermal Evaporation Source, (f) Ion Plating with a Sputtering Source, (g) Ion Plating with an Arc Vaporization Source, and (h) Ion Beam-Assisted Deposition (IBAD) with a Thermal Evaporation Source and Ion Bombardment from an Ion Gun

taken from Donald Mattox, Introduction in Handbook of Phys. Vapor Depos. Processing, 2010 (2nd ed.)

3.2 Thermodynamics of Vaporization: $p_v(T)$

Different evaporation situations:

- (a) vapor-liquid (or solid) equilibrium situation in a closed isothermal container
- (b) Knudsen-cell effusion
- (c) vacuum evaporation



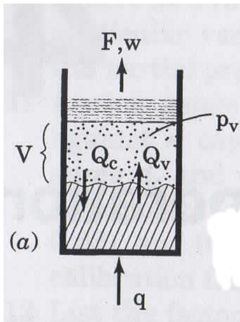
p_v - (saturation) vapor pressure,
q - heat
w - mechanical work
F - force
Q_c - molar condensation rate
Q_v - molar evaporation rate

Objective of the section: predict the dependence of vapor pressure on temperature
(in closed isothermal container)

Closed isothermal container - determination of $p_v(T)$

Consider

- a single element or a pure compound that does not dissociate upon evaporation,
- vapor-liquid (or solid) equilibrium in a closed isothermal container (pressure is p_v): **molar condensation rate Q_c and molar evaporation rate Q_v are balanced**.



The system is closed (no mass crossing) but

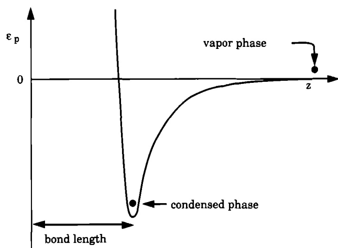
- **energy in a form of heat q** can be added causing evaporation
- **energy in the form of mechanical work $w = p_v \Delta V$** is removed from the resulting vapor as it pushes back the surrounding atmosphere (the piston)
- Not all of the heat input can be transformed into the work, most is **consumed in increasing the internal energy U** (1st law of thermodynamics)

$$\delta q = \delta w + \mathrm{d}U \tag{1}$$

Internal energy U

The 1st law of thermodynamics

$$dU = \delta q - \delta w \quad (1)$$



Parts of U

- **kinetic internal energy** (discussed in chapter 2, heat capacity)
- **molecular potential energy E_p** - accompanies removal of molecules from condensed phase into vapor phase

Entropy S

To further discuss equilibrium, we need to invoke the concept of entropy S.

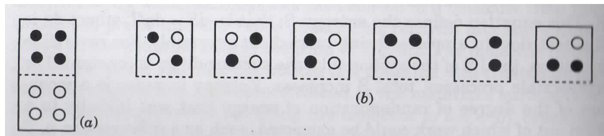
Consider a process involving slow changes in T and p, i.e. carried out close to equilibrium, and let the system be brought back to its original state - **reversible process**

The 2nd law of thermodynamics

$$\oint \frac{\delta q}{T} = \oint \mathrm{d}S = 0 \qquad (2)$$

In reversible process, S does not increase because it is already as high as it can be (given the amount of energy available).

irreversible mixing: increase of S is a measure of the degree of randomization of the energy



$\Rightarrow$ increase of entropy from 0 to $1.79k_\mathrm{B}$

$$S = k_\mathrm{B} \ln \Sigma \qquad (3)$$

where Σ is the number of quantum states. *Reason for* $\ln \Sigma$*: S appears in energy terms and energy is additive (whereas probability terms are multiplicative).*

In spontaneous processes, entropy always increases.

Gibbs Free Energy

- At fixed energy, entropy tends towards a maximum as the system approaches equilibrium.
- At fixed entropy, energy tends towards a minimum as the system approaches equilibrium.

In evaporation, and many other processes, both energy and entropy are varying:

- Removal of the molecule from the potential well into the vapor phase **increases its potential and kinetic energy**.
- It **increases also entropy because the molecule in vapor phase has more quantum states** available to it, both in position ("configurational" entropy - because it is in free space) and in energy levels ("thermal" entropy - because the translational-energy quantum states are so closely spaced).

The equilibrium relationship between the competing factors of energy and entropy is given by Eq. (1) in which $\delta w = pdV$ and $\delta q = TdS$

$$\mathrm{d}U + p\mathrm{d}V - T\mathrm{d}S = \mathrm{d}G = 0 \tag{4}$$

where **Gibbs free energy** G is introduced as

$$G = U + pV - TS. \tag{5}$$

Thermodynamic Quantities - Energy Terms

Gibbs free energy:

$$G = (U + pV) - TS = H - TS. \qquad (6)$$

where H is **enthalpy** that appeared earlier in connection to heat capacity at constant p.

- The **enthalpy** H is the energy term used for processes at constant p, where $p\mathrm{d}V$ work is being done on the surroundings.
- The **internal energy** U would be used for processes at constant V.

Recall

$$c_\mathrm{V} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V \qquad c_\mathrm{p} = \left(\frac{\partial H_\mathrm{m}}{\partial T}\right)_p$$

Differentiating Eq. (6), we have

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + \mathrm{d}pV - T\mathrm{d}S - \mathrm{d}TS \qquad (7)$$

It reduces to Eq. (4) for **processes at constant T and p** (such as evaporation and many other processes in thin-film work):

$$\mathrm{d}U + p\mathrm{d}V - T\mathrm{d}S = \mathrm{d}G = 0, \qquad (8)$$

$\Rightarrow$ **Gibbs free energy G** provides a concise definition of equilibrium:

System held at constant p and T is at equilibrium when $\mathrm{d}G = 0$ (G is at minimum).

Chemical Potential

$G = U - TS + pV$, where TS represents a "thermal" energy, pV a "mechanical" energy, and **G is a "chemical" energy $G = \mu N_\mathrm{m}$** (where N_m is number of moles).

$\Rightarrow$ Now, we have a complete expression for the **internal energy $U = TS - pV + \mu N_\mathrm{m}$**

Generalizing for a **multicomponent mixtures**:

$$G = \mu N_\mathrm{m} = \mu_1 N_\mathrm{m1} + \mu_2 N_\mathrm{m2} + \ldots, = \sum_i \mu_i N_\mathrm{mi} \quad (9)$$

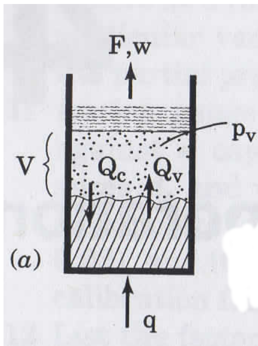
where μ_i is the **chemical potential of component i**,
$N_{\mathrm{m}i}$ is the number of moles of component i.

The chemical potential of component i is an incremental change in G for addition of material to a phase at constant T and p

$$\mu_i = \left(\frac{\partial G}{\partial N_{\mathrm{m}i}}\right)_{T,p,N_{\mathrm{m}j}} \quad (10)$$

For a **single-component system**, such as evaporating pure condensate,
μ is just the free energy per mole of condensate, G_mc.

Finding Dependence of Vapor Pressure p_v on T



At vapor-liquid equilibrium of closed vapor + liquid system, $G = \mathrm{const}$
(as evaporation proceeds at constant T and p) $\Rightarrow$

$$\mu_\mathrm{c} = \mu_\mathrm{v} \tag{11}$$

where c and v denote the condensed and vapor phases.

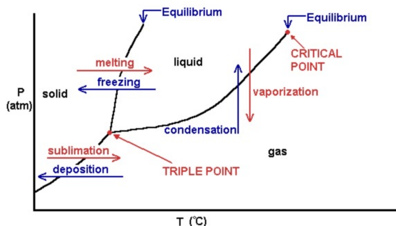
This is another way of stating the equilibrium conditions - number of moles of each component is constant (no reaction).

During evaporation, $H\uparrow$ but it is compensated by $S\uparrow$.

$$G = (U + pV) - TS = H - TS$$

At higher T, the entropy term TS becomes more important (increasing thermal motion produces randomization) $\Rightarrow$ more H can be compensated

Finding Dependence of Vapor Pressure $p_{\rm v}$ on T



- At any point along vapor-liquid (or solid) equilibrium curve $\mu_{\rm c} = \mu_{\rm v}$ holds.
- As we move up the curve, μ values of both phases increases

$\Rightarrow \mathrm{d}\mu_{\rm c} = \mathrm{d}\mu_{\rm v}$

or $\mathrm{d}G_{\rm mc} = \mathrm{d}G_{\rm mv}$ for pure material

Using Eq. (7) and equilibrium conditions Eq. (4)

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T \quad \text{or} \quad \mathrm{d}G_{\rm mi} = V_{\rm mi}\mathrm{d}p - S_{\rm mi}\mathrm{d}T \tag{12}$$

where $i = \rm c, v$.

Thus, at equilibrium between the two phases

$$V_{\rm mc}\mathrm{d}p_{\rm v} - S_{\rm mc}\mathrm{d}T = V_{\rm mv}\mathrm{d}p_{\rm v} - S_{\rm mv}\mathrm{d}T \quad \Rightarrow \quad \frac{\mathrm{d}p_{\rm v}}{\mathrm{d}T} = \frac{S_{\rm mv} - S_{\rm mc}}{V_{\rm mv} - V_{\rm mc}} = \frac{\Delta S_{\rm m}}{\Delta V_{\rm m}} \tag{13}$$

Since $\Delta G_{\rm m} = 0$ for evaporation and $G = H - TS \Rightarrow \Delta_{\rm V} H = T\Delta S_{\rm m}$ where $\Delta_{\rm V} H$ is the "**latent heat**" (enthalpy change) **of vaporization per mole**.

Clausius-Clapeyron Equation, i. e. $p_v(T)$

The heat of vaporization is an H term rather than a U term because it is measured at constant p, not constant V and, thus, it includes the $p\Delta V$ work of expansion.

Substituing $\Delta_V H/T$ for $\Delta S_m = S_{mv} - S_{mc}$ in Eq. (13) leads to **Clausius-Clapeyron equation:**

$$\frac{dp_v}{dT} = \frac{\Delta_V H}{T\Delta V_m} \tag{14}$$

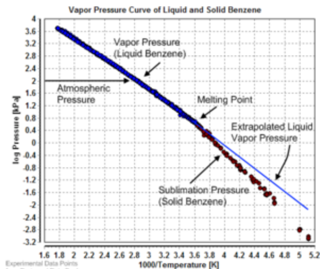
The volume term $\Delta V_m = V_{mv} - V_{mc}$ may be eliminated as follows:

- V_{mc} is negligible - it is typically $1/1000\,V_{mv}$ at 1 atmosphere
- for ideal gases $V_{mv} = RT/p$

$$\frac{dp_v}{p_v} = \left(\frac{\Delta_V H}{RT^2}\right) dT \tag{15}$$

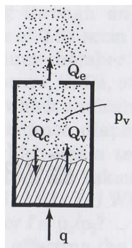
$$p_v = B\exp(-\Delta_V H/RT) \tag{16}$$

This **exponential expression** is familiar from all thermally activated chemical processes, evaporation being an example.
It is very **useful for estimation of p_v** if $p_v(T)$ data are not available.



3.3 Evaporation Rate - Expression of Effusion Rate Q_e

Objective: determine the evaporation rate of a material from available data such as the boiling point and heat of evaporation.



Closed system from previous discussion is modified by opening an orifice, which is small enough $\Rightarrow Q_\mathrm{e}$ does not significantly reduce the pressure, i.e. $p \approx p_\mathrm{v}$.

- For orifice with small diameter L, $Kn = \lambda/L > 1$, i.e. molecular-flow regime.
- If the orifice length $\ll$ orifice diameter (ideal orifice) the **effusion rate** Q_e can be easily derived.

The mass flow or throughput Q is usually expressed in Pa.l/s

$$Q = C\delta p \tag{17}$$

where C is conductance, δp is the pressure difference across the element.
For molecular flow, the flux through the orifice in each direction is the flux at the plane of orifice (A is the area of orifice)

$$\Gamma_i = \frac{p}{\sqrt{2\pi k_\mathrm{B} T m}} \quad \Rightarrow \quad Q = (\Gamma_2 - \Gamma_1)A = (p_2 - p_1)\frac{A}{\sqrt{2\pi k_\mathrm{B} T m}} = (p_2 - p_1)C \tag{18}$$

Close to vapor-liquid (or solid) equilibrium, the effusion rate Q_e from the **Knudsen cell** (vapor source with small orifice, outside pressure negligible $p_1 \approx 0$) can be found just from the vapor pressure p_v:

$$Q_\mathrm{e} = p_\mathrm{v}\frac{A}{\sqrt{2\pi k_\mathrm{B} T m}} \tag{19}$$

Evaporation Rate Q_v

After determining Q_e we want to express **the evaporation rate from the surface of the condensed phase, Q_v**. For the **Knudsen cell** (pressure should stay p_v)

$$Q_\mathrm{e} \ll Q_\mathrm{v} \tag{20}$$

How to determine Q_v? We can reliably **determine an upper limit of Q_v**. In steady state

$$Q_\mathrm{v} = Q_\mathrm{c} + Q_\mathrm{e} \tag{21}$$

and Q_e can be neglected, i. e. , $Q_\mathrm{v} \approx Q_\mathrm{c}$ and we can write the same balance in terms of fluxes per unit area $\Gamma_\mathrm{v} \approx \Gamma_\mathrm{c}$ ($\Gamma_\mathrm{v} = Q_\mathrm{v}/A$).

Upon impingement, there is a range of interations with condensate surface (analyzed in chapter 4 - adsorption, deposition):

- everything is reflected - lower limit,
- **everything impinging condenses** $\Gamma_\mathrm{c} = \Gamma_\mathrm{i}$ & consider vapor-liquid equilibrium $\Rightarrow$

$$\Gamma_\mathrm{i} = \Gamma_\mathrm{v0} = \frac{p_\mathrm{v}}{\sqrt{2\pi k_\mathrm{B} T m}} \tag{22}$$

  where Γ_v0 denotes the upper limit.

We expect that Γ_v0 is unchanged if we remove the vapor phase and consider evaporation from an **open crucible** (justification: evaporation of individual molecule of condensate is not retarded by the impingement of vapor molecules).

Evaporation and Condensation Coefficient

It has been verified experimentally that **evaporation occurs at the upper limit Γ_{v0}** (0 for upper limit) for those **metals that have atomic vapors** (most metals).

For other materials $\Gamma_{\mathrm{v}} < \Gamma_{\mathrm{v0}}$ and emipirically

$$\Gamma_{\mathrm{v}} = \alpha_{\mathrm{v}} \Gamma_{\mathrm{v0}} \qquad (23)$$

where α_{v} is **evaporation coefficient**.

There is a corresponding **condensation coefficient α_{c}**

$$\Gamma_{\mathrm{c}} = \alpha_{\mathrm{c}} \Gamma_{\mathrm{i}} \qquad (24)$$

At equilibrium $\Gamma_{\mathrm{c}} = \Gamma_{\mathrm{v}} \quad \Rightarrow \quad \alpha_{\mathrm{c}} = \alpha_{\mathrm{v}}$. Otherwise they are different functions of p, T.

The coefficient α_{v} has been determined only for few materials, e.g. 10^{-4} for As. Generally, it is not known.

$\Rightarrow$ **Unless evaporation is being carried out from the Knudsen cell, effusion rate cannot be predicted accurately and must instead be measured directly in thin-film deposition process.**

3.4 Alloys - Partial Pressures

Multicomponent materials bring additional complication - the composition of the vapor phase generally differs from that of the condensed phase. Different approach for

- **alloys** - a solid solution or a mixture of solid phases, its composition is variable over a wide range. Examples: solder alloy Pb_xSn_{1-x},
- **compounds** - specific ratio of elements (stoichiometry), e.g. GaAs, SiO_2. **Dissociatively evaporating compounds** - discussed in next section.
- alloy of compounds, e.g. $(AlAs)_x(GaAs)_{1-x}$

Consider a generalized **binary metal alloy B_xC_{1-x}** (well mixed liquid phase) whose component elements B and C are completely miscible at the evaporation T, i.e. atomic fraction x can vary from 0 to 1 without precipitating a second solid phase.

Total equilibrium vapor pressure over the melt

$$p_{\mathrm{v}} = p_{\mathrm{B}} + p_{\mathrm{C}} \quad p_{\mathrm{B}} = a_{\mathrm{B}} x p_{\mathrm{vB}} \quad p_{\mathrm{C}} = a_{\mathrm{C}}(1-x) p_{\mathrm{vC}} \tag{25}$$

where p_{vB}, p_{vC} are p_{v} of pure elements and $a_{\mathrm{B,C}}$ are the **activity coefficients**.

For simplicity, “Raoult’s law” behaviour is assumed, i.e. $a_{\mathrm{B,C}} = 1$, even though they generally deviate somewhat from unity due to differences between B-C versus B-B and C-C bond strengths.

Flux Ratio

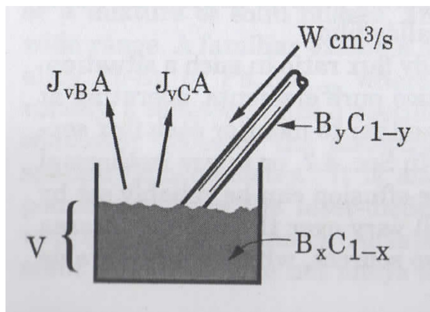
If the evaporation coefficients $\alpha_{\mathrm{vB,C}}$ are unity (common for metals) the ratio of evaporation fluxes is

$$\frac{\Gamma_{\mathrm{vB}}}{\Gamma_{\mathrm{vC}}} = \frac{x}{1-x}\frac{p_{\mathrm{vB}}}{p_{\mathrm{vC}}}\sqrt{\frac{m_{\mathrm{C}}}{m_{\mathrm{B}}}} \tag{26}$$

The vapor flux will be richer that the melt in the more volatile element for any composition x.

It leads to continuous changes of the melt composition until the equilibrium is reached (time consuming). The problem has two possible solutions:

1. use separate sources operating at different T levels
2. feed an alloy B_yC_{1-y} wire or rod steadily into the melt during evaporation



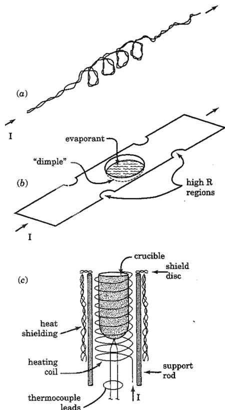
3.4 Compounds

Compounds behave very differently from alloys during evaporation:

- some compounds evaporate as molecules (ionically bonded compounds, e.g. MgF_2 for antireflective coating) - similar as single-component material
- dissociative evaporation - oxides vary in behaviour, SiO_2 evaporates as SiO in the presence of reducing agent Si, C, H_2

3.5 Sources for thermal evaporation - Resistive Heating

Několik typů zdrojů pro napařování využívajících ohřevu průchodem elektrického proudu:



- **Přímé odporové zahřívání** - Tato metoda je založena na ohřívání materiálu držáku z odporového, těžko tavitelného materiálu, jako je W, Mo, Ta, Nb. Někdy se používá i keramické úpravy povrchu těchto držáků. Tyto zdroje můžeme dále dělit podle tvaru držáku, a tedy způsobu uchycení taveného materiálu.
  - Drátěný držák má formu spirály. Odpařovaný materiál ve tvaru svorky U je na spirále zavěšen. Odpařovaný materiál musí smáčet spirálu, aby se na něj po roztavení nalepil.
  - Drátěný držák má tvar košíku. Napařovaný materiál nesmí košík smáčet, aby po roztavení vytvořil kapku, která nevyteče.
  - Držák má tvar plechové lodičky, v níž je odpařovaný materiál vložen. Lodička je přibližně 0,3 cm hluboká, 10 cm dlouhá a 1 až 2 cm široká. Výkon potřebný pro tyto zdroje je podstatně větší, než v případě drátového uchycení, ale lze deponovat tlustší vrstvy.
  - Zdroj je realizován jako uzavřená pec s jedním nebo více malými otvory, kterými proudí napařovaný materiál.
- **Nepřímé odporové zahřívání** - Kelímek z křemene, grafitu nebo keramiky (např. korundu) je obtočen drátěnou odporovou spirálou.

Pokud má materiál dostatečně vysokou tenzi par před tavením, začne sublimovat a následné kondenzát vytváří tenkou vrstvu. Nevýhodou je nízká depoziční rychlost.

3.6 Sources using Energetic Beams

- **Jiskrové napařování** Rychlé napařování slitin, či několikasložkových sloučenin, které se normálně mají tendenci rozpadat na složky, lze dosáhnout kapáním malinkých kapek na horký povrch. Dojde tak k separátnímu odpařování na mnoha místech kdy se ale v každém místě odpaří všechny složky.
- **Obloukové napařování.** Zapálením elektrického oblouku mezi dvěma vodivými elektrodami dochází v místě dopadu oblouku k velkému ohřevu materiálu. Teplota je dostatečná i k odpařování Nb a Ta. Tato metoda je také často používá k napařování uhlíku na vzorky pro elektronový mikroskop.
- **Exploding wire method.** This technique is based on the explosion of the wire caused by rapid heating due to the passage of a large current density 10^4–10^6 A/mm^2. This effect is achieved by an array of capacitors ($\approx$ 10 to 100 μF) charged to a voltage of $\approx$ 1 to 10 kV. The energy consumption is about 25 kWh/kg. The wire is typically gold, aluminum, iron or platinum, and is usually less than 0.5 mm in diameter.
- **Laserové napařování** nebo spíše **Pulsed Laser Deposition - PLD.** Obrovská intenzita laserového svazku může být použita k ohřevu a odpařování materiálu. Laserový zdroj může být mimo vakuový systém a svazek bývá zaostřen na povrch napařovaného materiálu.
- **RF ohřev.** Pro ohřev materiálu lze použít elektromagnetickou indukci. Ohřev lze aplikovat buď přímo na napařovaný materiál, nebo nepřímo na kelímek v němž je napařovaný materiál uložen.

3.6 Sources using Energetic Beams - Electron Beam Evaporation

Evaporation using resistance heating has a major disadvantage that the material being evaporated tends to be contaminated by the holder material. Also, the evaporation is limited by the input power (melting of the holder would occur), which makes evaporation of high melting temperature materials very difficult. This can be circumvented by electron beam evaporation.

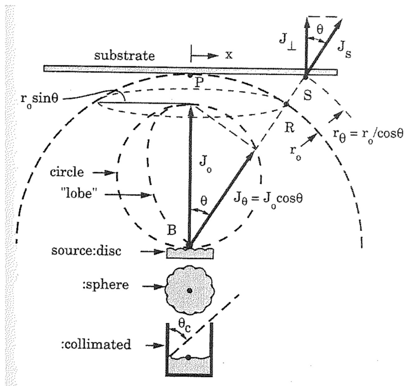
The simplest arrangement consists of a tungsten filament that is heated and emits electrons. These are then accelerated by applying a positive voltage to the material being evaporated. The electrons heat the material because they lose their energy there, causing it to evaporate.

For more details see scanned copy of Smith's book.

3.7 Transport

Transport = 2. step in the deposition process. Main issues:

- contamination - reason for high-vacuum operation
- arrival rate uniformity - analyzed with molecular flow $Kn = \lambda/L > 1$ where L is the distance from the source to substrate $\Rightarrow$ solely geometrical factors

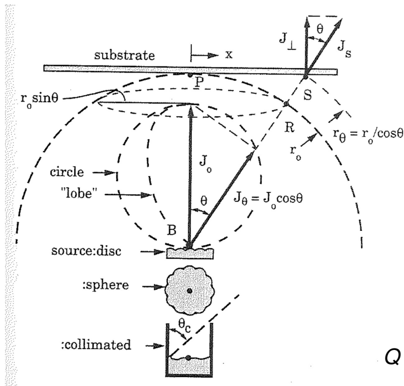


Different models of the source:

- circular disc - emitting material from the top surface only, represents the boat, Knudsen-cell orifice, filled crucible
- sphere - approximates wire-coil source
- collimated source - partly filled crucible or non-ideal orifice (orifice whose length $\gg$ its diameter)

3.7 Transport - Evaporant Flux Γ_θ

How to calculate **evaporant flux Γ_θ** at r_0? As projected area of the source in direction θ.



For sphere it is equal to perpendicular evaporation flux Γ_0:

$$\Gamma_\theta = \Gamma_0 = \frac{Q}{4\pi r_0^2} \tag{27}$$

where $Q = \Gamma_v A$ is total evap. rate from the source (Γ_v - emitting flux, A - area).

For disc:

$$\Gamma_\theta = \Gamma_0 \cos\theta \tag{28}$$

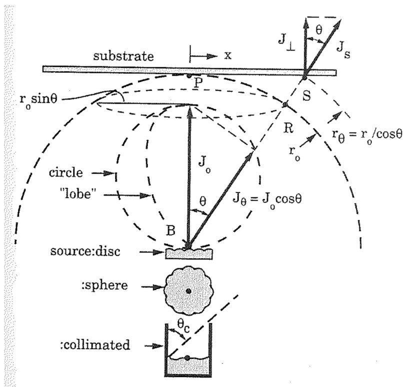
$\Gamma_0 = ?$

$$Q = \int_0^{2\pi} \int_0^{\pi} \Gamma_0 \cos\theta r_0^2 \sin\theta \mathrm{d}\theta \mathrm{d}\phi = \pi r_0^2 \Gamma_0$$

$$\Gamma_0 = \frac{Q}{\pi r_0^2} \tag{29}$$

For colimated source: more complicated - lobe distribution. Although there is some angle θ_c above which the evaporant source is not visible at all, there will be some flux at high angles because of evaporant scattering from the collimating sidewals.

3.7 Transport - Uniformity



For disc (simple cosine distribution)

Two factors have to be taken into account:

- substrate at point S is at radius $r_\theta = r_0/\cos\theta$

$\Rightarrow \Gamma_s = \Gamma_\theta \cos^2\theta \quad (\Gamma \sim 1/r^2)$

- flux that determines dep. rate is the flux perpendicular to the substrate ($\Gamma_\perp$) at point S

$$\Gamma_\perp = \Gamma_s \cos\theta$$

Finally,

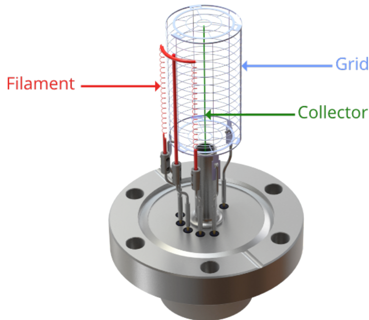
$$\Gamma_\perp = \Gamma_0 \cos^4\theta = \frac{Q\cos^4\theta}{\pi r_0^2} \qquad (30)$$

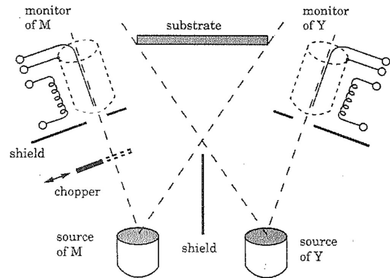
3.8 Monitoring of Deposition Process

Calculation of the vapor flux is complicated by uncertainity in the evaporation rates of the various species or due to the presence of the lobed flux distribution. The vapor flux is related to

- concentration of source vapor (**ion-gauge flux monitor**, mass spectrometer, electron-impact emission spectrometer)
- mass deposition - quartz crystal microbalance (QCM)
- thickness by optical methods - reflectance, ellipsometry

Ion gauge flux monitor = ion pressure gauge





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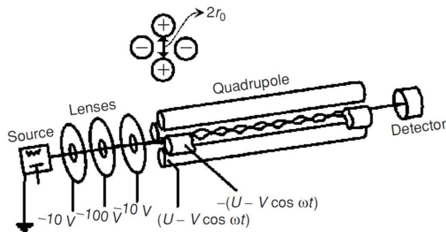
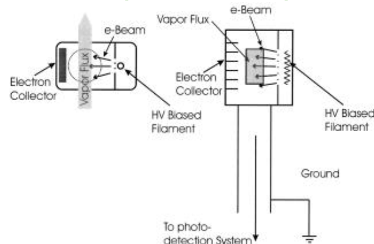
quadrupole mass spectrometer

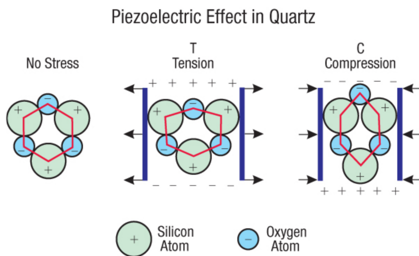


electron-impact emission spectrometer

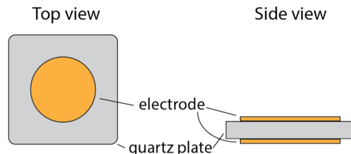


Quartz Crystal Microbalance (QCM)

QCM sensor is based on the **piezoelectric effect:**
A crystal under strain becomes electrically polarized. When deformed, the atoms are displaced, producing electrical dipoles in the material. In noninversion symmetry crystals, the summation of these dipoles generates dipole moments. The effect can be reversed by applying an electrical field to the crystal, and the internal mechanical strain is generated.



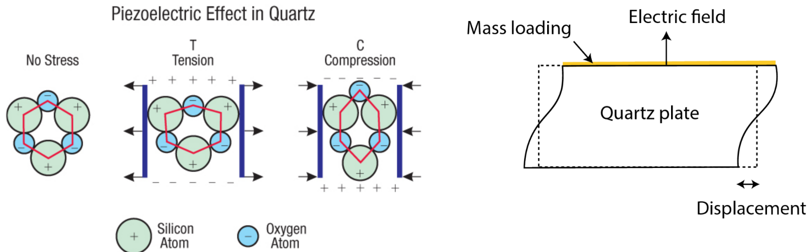
QCM structure: a pair of electrodes coupled with piezoelectric crystal, typically AT-cut quartz (SiO_2).



If an alternating electric field with a frequency close to the resonant frequency of the crystal plate is applied to the electrode, the crystal vibrates intensely and stably (high Q factor).

Quartz Crystal Microbalance (QCM)

The AT-cut quartz crystal operates at thickness-shear mode. The fundamental frequency of this crystal cut is typically 1–30 MHz.



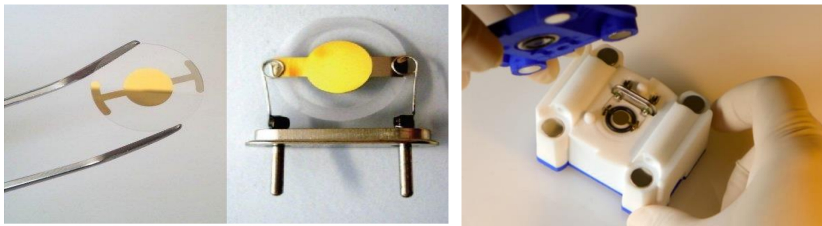
QCM is extremely sensitive to mass changes Δm in the nano-scale regime per unit area A

$$\Delta f = -\frac{2f_0^2}{\sqrt{\varrho E}}\frac{\Delta m}{A}$$

where f_0 is the fundamental frequency, ϱ and E are the crystal mass density and Young's modulus.
For quartz: $\varrho = 2.647$ g/cm^3 and $E = 2.947 \times 10^{11}$ dyn/cm^2

Quartz Crystal Microbalance (QCM)

Sensing can be active or passive.
The active or "oscillating" method requires connecting the sensor to an oscillator amplifier circuit providing a positive feedback. The piezoelectric crystal's oscilations can be measured using a frequency counter.



The change of frequency Δf gives the mass change Δm

$$\Delta f = -\frac{2f_0^2}{\sqrt{\varrho E}}\frac{\Delta m}{A}$$

The film thickness can be determined from the film density and the gold electrode area.