

F4280 Technologie depozice tenkých vrstev a povrchových úprav

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). It is composed of three subsequent steps:

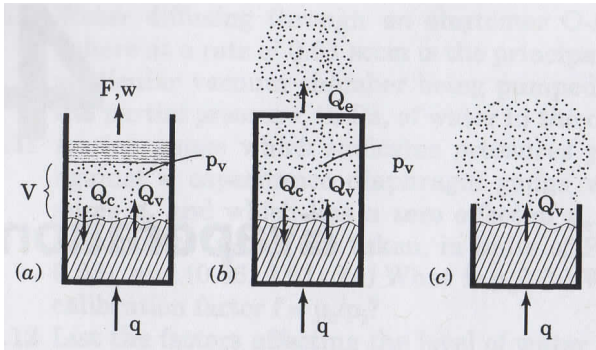
1. Obtaining the vapors of solid materials (vaporization) that do not have high enough vapor pressure \Rightarrow material have to be heated to so high temperatures that they melt and evaporate at sufficiently high vapor pressure.
2. Transport of vapors from the source to the substrate.
3. Condensation 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.
- ▶ 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 vacuum evaporation.
- ▶ Vacuum evaporation of metallic thin films was not common until 1920s.

3.2 Thermodynamics of Vaporization

Objective of this section is to predict the dependence of vapor pressure on temperature. In the next section, the evaporation rate of a material will be determined from available data such as the boiling point and heat of evaporation.



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

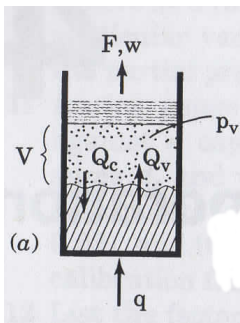
Different evaporation situations:

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

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

Consider either a single element or a pure compound that does not dissociate upon evaporation.

Vapor-liquid (or solid) equilibrium situation in a closed isothermal container: the 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)

$$dU + dw = dq \quad (1)$$

Parts of U

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

Entropy

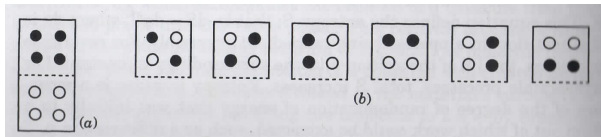
To further discuss equilibrium, we need to invoke the more subtle concept of entropy S .

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**

$$\oint \frac{dq}{T} = \oint dS = 0 \quad (2) \quad \text{obeying 2nd law of thermodynamics - } S \text{ does not increase because it is already as high as it can be given the amount of energy available}$$

irreversible mixing:

increase of S is a measure of the degree of randomization of the energy



$$S = k_B \ln \Sigma \quad (3) \quad \Rightarrow \text{increase of entropy from } 0 \text{ to } 1.79k_B$$

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).

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 $dw = pdV$ and $dq = TdS$

$$dU + pdV - TdS = dG = 0 \quad (4)$$

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

$$G = (U + pV) - TS = H - TS. \quad (5)$$

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

Thermodynamic Quantities - Chemical Potential

- ▶ The enthalpy H is the energy term used for processes at constant p , where $p dV$ work is being done on the surroundings.
- ▶ The internal energy U would be used for processes at constant V .

Diiferentiating Eq. (5), we have

$$dG = dU + p dV + dpV - T dS - dTS \quad (6)$$

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

$$dU + p dV - T dS = dG = 0, \quad (7)$$

⇒ **System held at constant p and T is at equilibrium when $dG = 0$ (G is at minimum) for any disturbance such as evaporation of dN_m moles of condensate.**

Chemical Potential

Incremental change in G for addition of material to a phase at constant T and p (**applied to multicomponent mixtures**)

$$\mu_i = \left(\frac{\partial G}{\partial N_{mi}} \right)_{T,p,N_{mj}} \quad (8)$$

where μ_i is **chemical potential of component i** , N_{mi} is the number of moles of component i .

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

We have shown that at vapor-liquid equilibrium of closed vapor + liquid system, $G = \text{const}$ (as evaporation proceeds at constant T and p) \Rightarrow

$$\mu_c = \mu_v \quad (9)$$

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).

Dependence of Vapor Pressure p_v on T

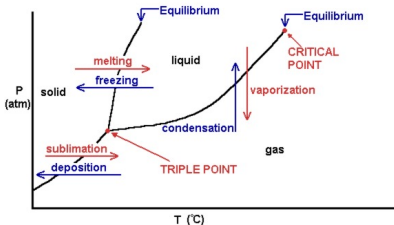
During evaporation, $H \uparrow$ but it is compensated by $S \uparrow$.

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

At higher T , the entropy term TS becomes more important (increasing thermal motion produces randomization) \Rightarrow more H can be compensated & we know p_v increases with T

Evaporation can proceed by absorption of heat from surroundings (evaporative cooling), which creates a T difference. Then, it is driven by $S \uparrow$ accompanying the evaporation \Rightarrow example of **endothermic** (heat absorbing) reaction.

Dependence of Vapor Pressure p_v on T



- ▶ At any point along vapor-liquid (or solid) equilibrium curve $\mu_c = \mu_v$ holds.
- ▶ As we move up the curve, μ values of both phases increases

$$\Rightarrow d\mu_c = d\mu_v$$

$$\text{or } dG_{mc} = dG_{mv} \text{ for pure material}$$

Using Eq. (6) and equilibrium conditions Eq. (4)

$$dG = Vdp - SdT \quad \text{or} \quad dG_{mi} = V_{mi}dp - S_{mi}dT \quad (10)$$

where $i = c, v$.

Thus, at equilibrium between the two phases

$$V_{mc}dp_v - S_{mc}dT = V_{mv}dp_v - S_{mv}dT \quad \Rightarrow \quad \frac{dp_v}{dT} = \frac{S_{mv} - S_{mc}}{V_{mv} - V_{mc}} = \frac{\Delta S_m}{\Delta V_m} \quad (11)$$

Since $\Delta G_m = 0$ for evaporation and $G = H - TS \Rightarrow \Delta_v H = T\Delta S_m$ where $\Delta_v H$ 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.

Substituting $\Delta_V H/T$ for $\Delta S_m = S_{mV} - S_{mC}$ in Eq. (11) leads to **Clausius-Clapeyron equation**:

$$\frac{dp_v}{dT} = \frac{\Delta_V H}{T\Delta V_m} \quad (12)$$

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

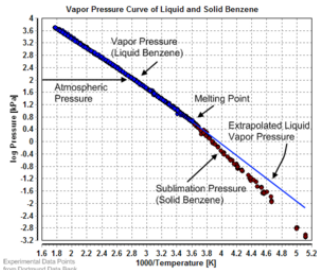
$$\frac{dp_v}{p_v} = \left(\frac{\Delta_V H}{RT^2} \right) dT \quad (13)$$

- ▶ V_{mC} is negligible - it is typically $1/1000 V_{mV}$ at 1 atmosphere
- ▶ for ideal gases $V_{mV} = RT/p$

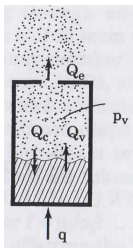
$$p_v = B \exp(-\Delta_V H/RT) \quad (14)$$

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 - Effusion Rate



Closed system from previous discussion is modified by opening an orifice, which is small enough $\Rightarrow Q_e$ does not significantly reduce the pressure, i.e. $p \approx p_v$.

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

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

$$Q = C\delta p \quad (15)$$

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)

$$\Gamma_i = \frac{p}{\sqrt{2\pi k_B T m}} \Rightarrow Q = (\Gamma_2 - \Gamma_1)A = (p_2 - p_1) \frac{A}{\sqrt{2\pi k_B T m}} = (p_2 - p_1)C \quad (16)$$

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 :

$$Q_e = p_v \frac{A}{\sqrt{2\pi k_B T m}} \quad (17)$$

Evaporation Rate Q_v (for Knudsen cell and metals with atomic vapors)

Since we do not want to reduce the pressure inside the cell,

$$Q_e \ll Q_v \quad (18)$$

where Q_v is evaporation rate from the surface of the condensed phase.

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

$$Q_v = Q_c + Q_e \quad (19)$$

and Q_e can be neglected $Q_v \approx Q_c$.

For determination of $Q_v = \Gamma_v/A$, we use the same **balance of impinging flux $\Gamma_v \approx \Gamma_c$** . Upon impingement, there is a range of interactions with condensate surface (analyzed in chapter 4 - adsorption, deposition):

- ▶ everything is reflected - lower limit,
- ▶ **everything impinging condenses** - upper limit $\Gamma_c = \Gamma_i$

$$Q_v = \frac{\Gamma_{v0}}{A} = \frac{\Gamma_i}{A} = \frac{p}{A\sqrt{2\pi k_B T m}} \quad (20)$$

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

Evaporation and Condensation Coefficient

Previous result on Q_v estimation was valid for Knudsen cell and metals with atomic vapors.

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).

For other materials $\Gamma_v < \Gamma_{v0}$ and empirically

$$\Gamma_v = \alpha_v \Gamma_{v0} \quad (21)$$

where α_v is **evaporation coefficient**.

There is a corresponding **condensation coefficient** α_c

$$\Gamma_c = \alpha_c \Gamma_i \quad (22)$$

At equilibrium $\Gamma_c = \Gamma_v \Rightarrow \alpha_c = \alpha_v$. 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.

3.3 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 .
- ▶ alloy of compounds, e.g. $(AlAs)_x(GaAs)_{1-x}$

Evaporation of compounds is discussed in next section.

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

$$p_v = p_B + p_C \quad p_B = a_B x p_{vB} \quad p_C = a_C (1 - x) p_{vC} \quad (23)$$

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

For simplicity, "Raoult's law" behaviour is assumed, i.e. $a_{B,C} = 1$, 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 are unity (common for metals) the ratio of evaporation fluxes is

$$\frac{\Gamma_{vB}}{\Gamma_{vC}} = \frac{x}{1-x} \frac{p_{vB}}{p_{vC}} \sqrt{\frac{m_C}{m_B}} \quad (24)$$

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

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

Existuje několik typů zdrojů pro napařování, které využívají 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** - Kelímeček z křemene, grafitu nebo keramiky (např. korundu) je obtočen drátěnou odporovou spirálou.

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

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

3.6 Sources using Energetic Beams

- ▶ **Jiskrové napařování** Rychlé napařování slitin, či několikasožkových 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.
- ▶ **Technika explodujícího drátu.** Tato technika je založená na explozi drátku způsobené prudkým ohřevem díky průchodu velkého proudu, řádově 10^6 A/cm². Takového efektu je dosaženo polem kondenzátorů (≈ 10 to $100 \mu\text{F}$) nabitým na napětí ≈ 1 to 10 kV.
- ▶ **Laserové napařování.** 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

- ▶ **Napařování elektronovým svazkem** Napařování použitím odporového zahřívání má velkou nevýhodu v tom, že napařovaný materiál bývá kontaminován materiálem držáku. Také je napařování limotováno vstupním výkonem (došlo by k tavení držáku), což značně ztěžuje napařování materiálů s vysokou teplotou tání. ⇒ lze to obejít pomocí elektronového bombardu materiálu.
Nejjednodušší uspořádání sestává z wolframového vlákna, které je žhaveno a emituje elektrony. Ty jsou následně urychlovány díky přivedení kladného napětí na napařovaný materiál. Elektrony v něm ztrácejí svou energii, čímž materiál ohřívají a dochází k jeho vypařování.

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

3.7 Transport

see scanned copy of Smith's book

3.8 Monitoring of Deposition Process

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

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