

# F4280 Technologie depozice tenkých vrstev a povrchových úprav

## 3. Evaporation

Lenka Zajíčková

Přírodovědecká fakulta & CEITEC, Masarykova univerzita, Brno  
lenkaz@physics.muni.cz

jarní semestr 2017



Central European Institute of Technology  
BRNO | CZECH REPUBLIC



# Outline - chapter 3. Evaporation

- 3.1 Introduction to Evaporation
- 3.2 Thermodynamics of Evaporation
- 3.3 Evaporation Rate
- 3.3 Alloys
- 3.4 Compounds
- 3.5 Sources for Thermal Evaporation
- 3.6 Sources using Energetic Beams
- 3.7 Transport
- 3.8 Monitoring of Deposition Process

## 3.1 Introduction to Evaporation

Vysokoteplotní, nebo vakuové napařování (čistě fyzikální proces) se skládá z několika po sobě jdoucích kroků:

1. Získání par vypařováním nebo sublimací kapalných nebo pevných materiálů  $\Rightarrow$  nutno zahřívat na dostatečně vysokou teplotu.
2. Transport par od zdroje k substrátu.
3. Kondenzace par v podobě tenké vrstvy na chlazeném substrátu.

Vytváření tenké vrstvy uhlíku napařováním bylo pravděpodobně poprvé pozorováno Edisonem. První nanášení tenkých vrstev roztavením drátu velkým proudem je historicky přisuzováno Faradayovi. První využití vakua pak Nahrwoldovi, Pohlovi a Pringsheimovi.

## 3.2 Thermodynamics of Evaporation

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

Vapor-liquid or vapor-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 work, most is consumed in increasing the internal energy  $U$

- ▶ 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

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

# Entropy

Consider a process involving slow changes in temperature and pressure ( $T$  and  $p$ ), i.e. carried out close to equilibrium. The system can be brought back to its original state - **reversible process** obeying

$$\oint \frac{dq}{T} = \oint dS = 0 \quad (2)$$

Increase of entropy  $S$  is a measure of the degree of randomization of energy that was initially in a form out of work could be extracted, such as a difference in  $p$ ,  $T$  or concentration.

If the work of the force exerted by the piston was not used to store mechanical energy but it was dissipated as heat (by friction) total  $S$  would increase.

$$S = k_B \ln \Sigma \quad (3)$$

where  $\Sigma$  is number of quantum states. Reason for  $\ln \Sigma$  - energy terms ( $S$ ) are additive whereas probability terms are multiplicative

Example of entropy increase involving a concentration difference:

$\Rightarrow$  increase of entropy from 0 to  $1.79k_B$

# 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) and in energy levels (“thermal” entropy).

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

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

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

Diifferentiating Eq. (5), we have

$$dG = dU + pdV + dpV - TdS - dTS \quad (6)$$

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

⇒ 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.

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) ⇒ more  $H$  can be compensated ⇒  $p_v$  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 ⇒ example of **endothermic** (heat absorbing) reaction.

# Chemical Potential

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

$$\mu_i = \left( \frac{\partial G}{\partial N_{mi}} \right)_{T,p,N_{mj}} \quad (7)$$

where  $\mu_i$  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,  $\mu$  is just the free energy per mole of condensate,  $G_{mc}$ .

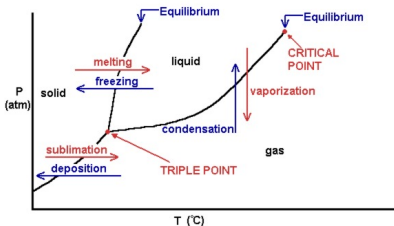
At vapor-liquid equilibrium of closed vapor + liquid system,  $G$  of the total system does not change as evaporation proceeds at constant  $T$  and  $p$

$$\mu_c = \mu_v \quad (8)$$

where c and v denote the condensed and vapor phases. In practice, the system must be slightly removed from equilibrium so that the heat of evaporation can flow into it along a  $T$  gradient.



# 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,  $\mu$  values of both phases increases

$$\Rightarrow d\mu_c = d\mu_v \text{ or } dG_{mc} = dG_{mv}$$

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

$$dG = Vdp - SdT \text{ or } dG_{mi} = V_{mi}dp - S_{mi}dT \quad (9)$$

where  $i = c, v$ .

Thus, at equilibrium between the two phases

$$V_{mc}dp_v - S_{mc}dT = V_{mv}dp_v - S_{mv}dT \Rightarrow \frac{dp_v}{dT} = \frac{S_{mv} - S_{mc}}{V_{mv} - V_{mc}} = \frac{\Delta S_m}{\Delta V_m} \quad (10)$$

## Clausius-Clapeyron Equation and $p_v$ on $T$

Since  $\Delta G_m = 0$  for evaporation, we have from  $G = H - TS$  that  $\Delta_V H = T\Delta S_m$  where  $\Delta_V H$  is the “**latent heat**” (enthalpy change) **of vaporization per mole**.

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. (10) leads to **Clausius-Clapeyron** eq.

$$\frac{dp_v}{dT} = \frac{\Delta_V H}{T\Delta V_m} \quad (11)$$

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

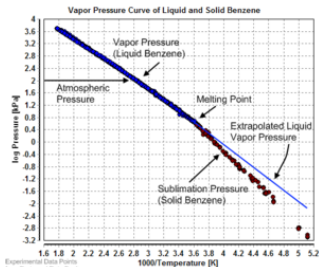
$$\frac{dp_v}{p_v} = \left( \frac{\Delta_V H}{RT^2} \right) dT \quad (12)$$

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

$$p_v = B \exp(-\Delta_V H/RT) \quad (13)$$

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

$$Q = C\delta p \quad (14)$$

where  $C$  is conductance,  $\delta p$  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)

$$\Gamma_i = \frac{p}{\sqrt{2\pi k_B T m}} \Rightarrow Q = (\Gamma_2 - \Gamma_1)A = (p_2 - p_1) \frac{A}{\sqrt{2\pi k_B T m}} = (p_2 - p_1)C \quad (15)$$

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  $p_v$ :

$$Q_e = p_v \frac{A}{\sqrt{2\pi k_B T m}} \quad (16)$$

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

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

$$Q_e \ll Q_v \quad (17)$$

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

$$Q_v = Q_c + Q_e \quad (18)$$

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  $\Gamma_c = \Gamma_i$

$$Q_v = \frac{\Gamma_{v0}}{A} = \frac{\Gamma_i}{A} = \frac{p}{A\sqrt{2\pi k_B T m}} \quad (19)$$

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  $\Gamma_{v0}$  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

$$\Gamma_v = \alpha_v \Gamma_{v0} \quad (20)$$

where  $\alpha_v$  is **evaporation coefficient**.

There is a corresponding **condensation coefficient**  $\alpha_c$

$$\Gamma_c = \alpha_c \Gamma_i \quad (21)$$

At equilibrium  $\Gamma_c = \Gamma_v \Rightarrow \alpha_c = \alpha_v$ . Otherwise they are different functions of  $p$ ,  $T$ .

The coefficient  $\alpha_v$  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

$$p_v = p_B + p_C \quad p_B = a_B x p_{vB} \quad p_C = a_C x p_{vC} \quad (22)$$

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

$$\frac{\Gamma_{vB}}{\Gamma_{vC}} = \frac{x}{1-x} \frac{\rho_{vB}}{\rho_{vC}} \sqrt{\frac{m_C}{m_B}} \quad (23)$$

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.  $\text{MgF}_2$  for antireflective coating) - similar as single-component material
- ▶ dissociative evaporation - oxides vary in behaviour,  $\text{SiO}_2$  evaporates as  $\text{SiO}$  in the presence of reducing agent Si, C,  $\text{H}_2$



## 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/cm<sup>2</sup>. Takového efektu je dosaženo polem kondenzátorů ( $\approx 10$  to  $100$   $\mu$ F) nabitým na napětí  $\approx 1$  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.