

Chap. 3 Thin-Film Evaporation Processes

3.1 INTRODUCTION

- **Evaporation** : deposition evaporation process is to controllably transfer atoms from a heated source to a substrate located a distance away, where film formation and growth proceed atomistically.
- **Sputtering**: another method for physically depositing films. In sputtering atoms are ejected from source surfaces usually maintained at room temperature, through the impact of gaseous ions.
- Physical vapor deposition(PVD) :
 - Reliance on solid or molten sources, as opposed to generally gaseous precursors in CVD
 - The physical mechanisms (evaporation or collisional impact) by which source atoms enter the gas phase
 - A reduced pressure environment through which the gaseous species are transported
 - The general absence of chemical reactions in the gas phase and at the substrate surface (reactive PVD processes are exceptions)

3.2 THE PHYSICS AND CHEMISTRY OF EVAPORATION

3.2.1 EVAPORATION RATE

$$\frac{\Phi}{N_A} = \frac{P}{(2\pi MRT)^{1/2}} \quad \text{moles/cm}^2\text{-s.}$$

$$\Phi_e = \frac{\alpha_c N_A (P_e - P_h)}{(2\pi MRT)^{1/2}}$$

P_e : equilibrium pressure
 P_h : hydrostatic pressure
 α_c : coefficient of evaporation

✓ ideal case
 if $\alpha_c = 1$ and $P_h = 0$
 $\Phi_e \rightarrow \text{max}$

$$\Phi_e = \frac{3.513 \times 10^{22}}{(MT)^{1/2}} P_e \quad \text{molecules/cm}^2\text{-s.} \quad ; P_e \text{ is expressed in torr}$$

$$\Gamma_e = 5.84 \times 10^{-2} (M/T)^{1/2} P_e \quad \text{g/cm}^2\text{-s.} \quad ; \Gamma_e : \text{mass evaporation rate}$$

$$\tau_e = f(P_e, \frac{1}{\sqrt{T}}, \frac{1}{\sqrt{M}})$$

Aluminum Example

- For Al, $M = 27$ gr
- From the vapor pressure diagram, to get $P_v = 10^{-4}$ Torr, we need to heat Al to 980 °C.
- At this temperature, the mass evaporation rate is:

$$\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{980}} 10^{-4} \frac{\text{gr}}{\text{cm}^2 \text{s}} = 9.694 \times 10^{-7} \frac{\text{gr}}{\text{cm}^2 \text{s}}$$

- If the vapor pressure is chosen to be 10^{-2} Torr, then the temperature has to be increased to 1220 °C and the evaporation rate becomes:

$$\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{1220}} 10^{-2} \frac{\text{gr}}{\text{cm}^2 \text{s}} = 8.688 \times 10^{-5} \frac{\text{gr}}{\text{cm}^2 \text{s}}$$

3.2.2 VAPOR PRESSURE OF THE ELEMENTS

- Clausius-Clayperon equation- both solid – vapor and liquid – vapor

In transformation process from vapor to condense phase

rate of equilibrium pressure to temperature, $\frac{dP}{dT}$

$$= \frac{\Delta H}{T \Delta V}$$

ΔH : change of enthalpy during transformation

ΔV : " " volume " "

T : transformation temperature between

vapor and condense phase

其中 $\Delta V = (V_v - V_c) \approx V_v$; $V_v \gg V_c$

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

ideal gas :: $pV_v = RT$; $V_v = \frac{RT}{p} \approx \Delta V$ $\left(\lambda \pm \lambda \right)$

$$\frac{dP}{dT} = \frac{\Delta H P}{T^2 R}$$

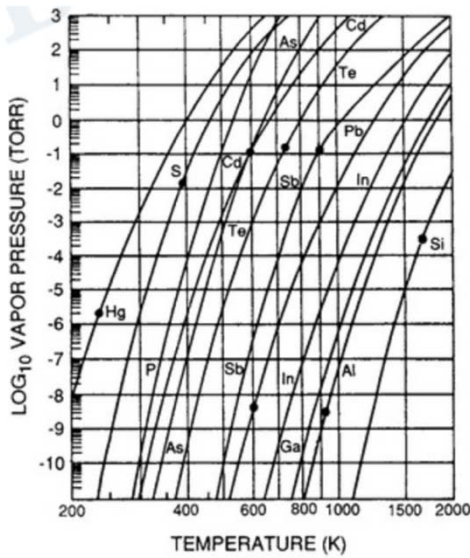
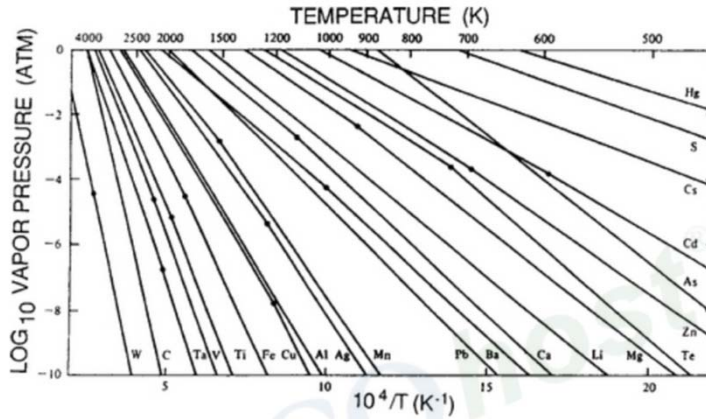
$$\int \frac{dp}{p} = \int \frac{\Delta H}{T^2 R} dT$$

$$\ln p = -\frac{\Delta H}{TR} + I \quad \leftarrow \text{constant of integration}$$

$$\ln p = -\left(\frac{\Delta H}{R}\right) \frac{1}{T} + I$$

$\Delta H = \text{latent heat of vaporization}$
 $T = \text{boiling point}$
 $P = 1 \text{ atm}$
 $\Rightarrow I = ?$

$y = m \cdot x + b$
 slope \nearrow interrupt \downarrow



Vapor pressures of elements employed in semiconductor materials

Two modes of evaporation (vapor pressure = 10^{-2} torr)

- ① evaporation temperature > melting point (for most metals)
- ② evaporation temperature < melting point (for Cr, Ti, Mo, Fe, Si)

3.2.3 EVAPORATION OF MULTIELEMENT MATERIALS

Table 3-1 Evaporation of Compounds

Reaction type	Chemical reaction ^a	Examples	Comments
Evaporation without dissociation	$\text{MX(s or l)} \rightarrow \text{MX(g)}$	SiO, B ₂ O ₃ , GeO, SnO, AlN, CaF ₂ , MgF ₂	Compound stoichiometry maintained in deposit
Decomposition	$\text{MX(s)} \rightarrow \text{M(s)} + \frac{1}{2}\text{X}_2(\text{g})$ $\text{MX(s)} \rightarrow \text{M(l)} + \frac{1}{n}\text{X}_n(\text{g})$	Ag ₂ S, Ag ₂ Se III-V semiconductors	Separate sources are required to deposit these compounds
Evaporation with dissociation			Deposits are metal-rich
(a) Chalcogenides	$\text{MX(s)} \rightarrow \text{M(g)} + \frac{1}{2}\text{X}_2(\text{g})$ X=S, Se, Te	CdS, CdSe, CdTe	Separate sources usually required to deposit these compounds
(b) Oxides	$\text{MO}_2(\text{s}) \rightarrow \text{MO(g)} + \frac{1}{2}\text{O}_2(\text{g})$	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)

^aM = metal, X = nonmetal.
Adapted from Ref. 4.

3.2.3.3 Evaporation of Alloys

- Evaporated metal alloy films are widely utilized for a variety of electronic, magnetic, and optical applications as well as for decorative coating purposes. Important examples of such alloys that have been directly evaporated include Al-Cu, Permalloy (Fe-Ni), Nichrome (Ni-Cr), and Co-Cr.

$$P_B = X_B P_B(0) \quad \begin{array}{l} P_B = \text{vapor pressure of component B} \\ X_B = \text{mole fraction} \\ P_B(0) = \text{vapor pressure of pure B} \end{array}$$

$$P_B = a_B P_B(0) \quad \begin{array}{l} a_B = \text{effective thermodynamic concentration of B} \\ \text{(activity)} \end{array}$$

$$a_B = \gamma_B X_B \quad \gamma_B = \text{activity coefficient}$$

$$\frac{\Phi_A}{\Phi_B} = \frac{\gamma_A X_A P_A(0) M_B^{1/2}}{\gamma_B X_B P_B(0) M_A^{1/2}}$$

$$; X_A + X_B = 1$$

Application of this equation is difficult because :

- Melt composition changes as evaporation proceeds
- Activity coefficients hard to find

Ex: Al-Cu Alloy Deposition

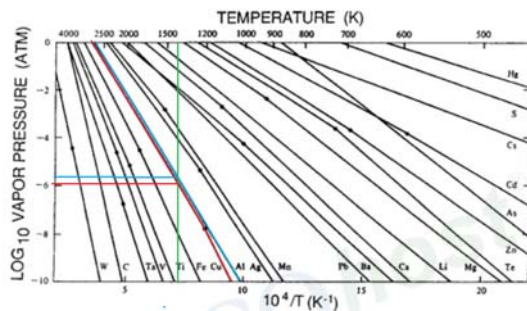
2wt% Cu from single crucible heated to 1350 K

$$\frac{\Phi_A}{\Phi_B} = \frac{\gamma_A X_A P_A(0) M_B^{1/2}}{\gamma_B X_B P_B(0) M_A^{1/2}}$$

$P_A(0), P_B(0)$

↓

$$\frac{X_A}{X_B} = \frac{\Phi_A}{\Phi_B} \cdot \frac{\gamma_B P_B(0) M_A^{1/2}}{\gamma_A P_A(0) M_B^{1/2}}$$



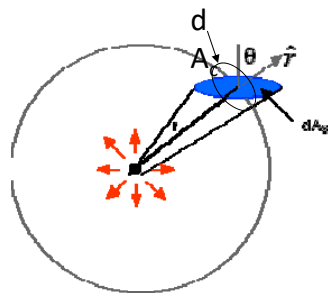
$$\frac{X_{Al}}{X_{Cu}} = \frac{98/27.0}{2/63.7} \cdot \frac{2 \times 10^{-4} (27.0)^{1/2}}{1 \times 10^{-3} (63.7)^{1/2}} = 15$$

All the original melt composition must be enriched to 13.6 wt% Cu.

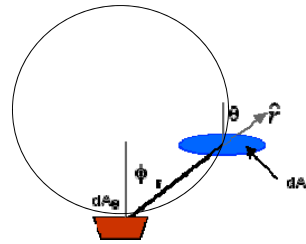
3.3 FILM THICKNESS UNIFORMITY AND PURITY

3.3.1 DEPOSITION GEOMETRY

Evaporation Source



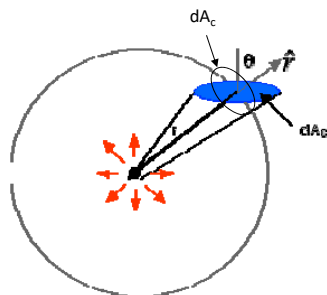
Point source



Surface source

www.imeng.ndhu.edu.tw/ezfiles/29/.../pta_18056_9804637_54886.ppt

Point Source $n = 0$



$$dA_c = dA_s \cos \theta$$

$$d\bar{M}_s : \bar{M}_e = dA_c : 4\pi r^2$$

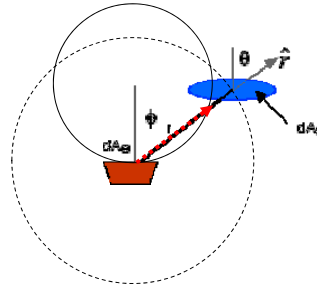
$$\frac{d\bar{M}_s}{dA_s} = \frac{\bar{M}_e \cos \theta}{4\pi r^2}$$

$d\bar{M}_s$: mass falls on the substrate of dA_s

\bar{M}_e : total evaporated mass

Knudsen Cell or Effusion Cell $n=1$

Cosine distribution flow through a hole



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