

# Thin films growth and deposition techniques

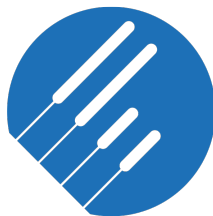
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## It-fab

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Italian Network for  
Micro and Nano Fabrication



**polifab**  
POLITECNICO DI MILANO

1. Introduction to thin films growth
2. Surface adsorption
3. Surface tension
4. Homogeneous nucleation
5. Heterogeneous nucleation
6. Strain effects
7. Growth modes
8. Coalescence processes
9. Deposition techniques
10. Evaporation

**Credits:**

Matteo Cantoni

Slides of the Course on Micro and Nanofabrication held at Politecnico di Milano - Polifab

## How growth takes place?

Condensation of atomic clusters on the substrate



Film thickening due to additional deposition



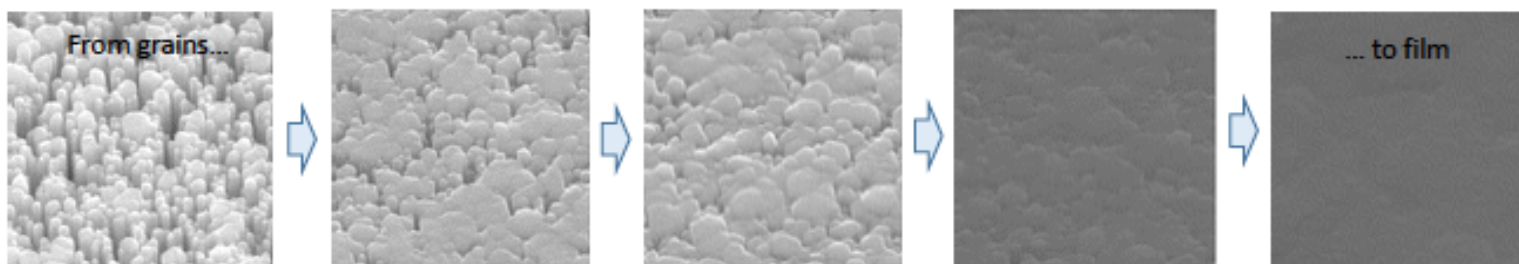
Fully developed single-crystals (SC), polycrystals (PC) or amorphous films



Relationships between film structure and growth process



Understanding properties of the deposited films



Es. ZnO on sapphire ( $\text{Al}_2\text{O}_3$ )

Reference for this lecture: M. Ohring, Materials Science of Thin films, Academic Press, Chapters 1 and 7

# Surfaces: adsorption reactions

- What happens when a surface is **exposed** to gas particles?

➔ **Surface adsorption** – impinging atoms and molecules enter and interact within the **transition region** between the gas phase and the surface.

## Physisorption (physical adsorption)

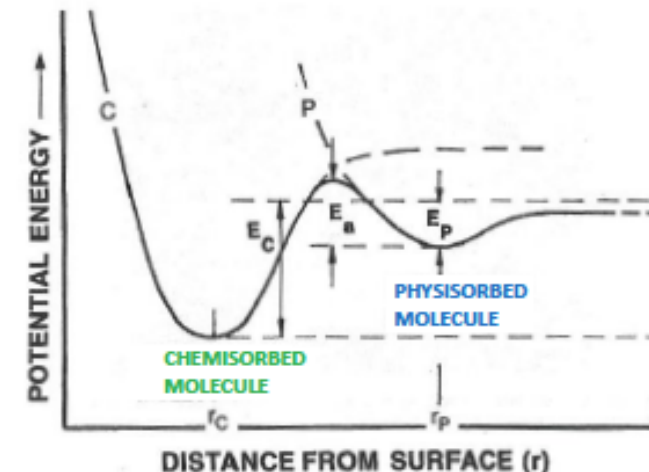
the particle is stretched or bent, but **retains its identity**; van der Waals forces bond it to the surface

## Chemisorption (chemical adsorption)

the particle **changes its identity** through ionic or covalent bonding with surface atoms

Note that:

- $r_p > r_c \Rightarrow$  P particles achieve equilibrium **further from the surface** than C ones
- $E_p (\sim 0.25 \text{ eV}) \ll E_c (\sim 1-10 \text{ eV}) \Rightarrow$  very different adsorption heats (or energies)
- Dissociation**: dissociative **chemisorption** is possible if  $E_{dis} < E_c$
- When both P and C occur, the transition rate from P to C is governed by the **effective energy**  $E_a$
- In the following we will use a **composite energy of adsorption** (integrated over all adsorption states)  $E_{ads}$ , and correspondingly a **composite energy of desorption** (integrated over all desorption states)  $E_{des}$



Model of physisorption (P) and chemisorption (C) processes in terms of the interaction potential between adsorbate and surface vs. the distance from the surface (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

# Surfaces: adsorption effects (1)

*How the surface adsorption and desorption energies influence film growth?*

- Consider a vapor phase containing adatoms at partial pressure  $P$ , that will condensate on a **substrate surface** (or the surface of a film previously grown, with the same hypothesis of cleanliness and sharpness)
- The net time rate of the substrate coverage  $\theta$  is given by:

$$\frac{d\theta}{dt} = k_{ads} P (1 - \theta) - k_{des} \theta$$

where:

- $\theta = 0$  means no coverage,  $\theta = 1$  means one monolayer (1 ML) coverage
- The first term is the **rate of adatoms coverage at the unoccupied surface sites** ( $1 - \theta$ ); it is proportional to the partial pressure  $P$  and the **absorption rate** constant, that depends on the composite **adsorption energy** as:

$$k_{ads} \sim \exp(-E_{ads}/k_B T) \Rightarrow k_{ads} \text{ increases when } E_{ads} \text{ decreases}$$

- The second term is the **rate of adatoms desorption from the occupied surface sites** ( $\theta$ ); it is proportional to the **desorption rate** constant, that depends on the composite **desorption energy** as:

$$k_{des} \sim \exp(-E_{des}/k_B T) \Rightarrow k_{des} \text{ decreases when } E_{des} \text{ increases}$$

## Surfaces: adsorption effects (2)

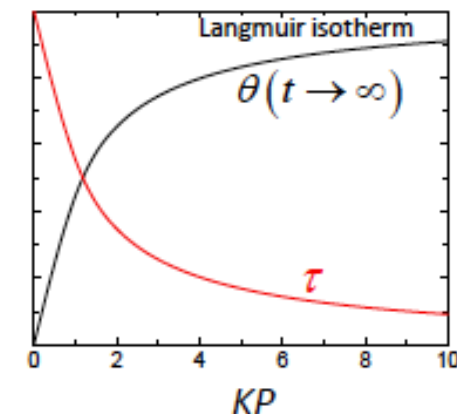
$$\frac{d\theta}{dt} = k_{ads}P(1-\theta) - k_{des}\theta \quad \Rightarrow \quad \text{The solution is: } \theta(t) = \frac{KP}{1+KP} \left[ 1 - \exp(-k_{des}(1+KP)t) \right], \text{ with } K = k_{ads}/k_{des}$$

Note that:

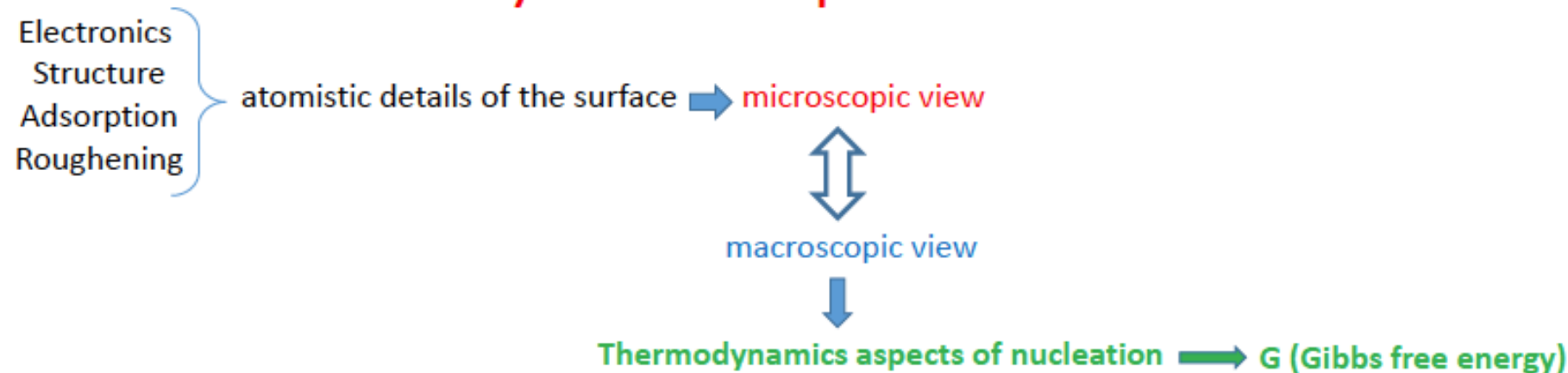
- If  $t \rightarrow \infty$  (or  $t \gg \tau$ , with  $\tau = [k_{des}(1+KP)]^{-1}$ )  $\Rightarrow \theta(t) \approx \frac{KP}{1+KP}$  (Langmuir isotherm)

- If  $KP \gg 1 \Rightarrow \begin{cases} \theta(t) \approx 1 \text{ (the surface is covered by one monolayer of adatoms)} \\ \tau \approx [k_{des}KP]^{-1} = [k_{ads}P]^{-1} \rightarrow 0 \end{cases}$

(  $KP = \frac{k_{ads}}{k_{des}} P \gg 1$  means large  $P$  and/or  $k_{ads} \gg k_{des}$  )  
 ( $E_{ads} \ll E_{des}$ )



## Thermodynamics aspects of nucleation



- **Nucleation** involves the creation a **new phase**, with generally **different** structure and/or composition (es. a solid phase), from a previously stable phase (es. a vapor phase) when critical boundaries between stable phase fields in equilibrium phase diagram are crossed (e.g. by decreasing the temperature, triggering the condensation process).
- **Nucleation** occurs during the **very early stages** of phase change, but have **a strong influence on the grain structure** that ultimately develops in a deposition process.
- Nucleation concerns the formation a **single stable nucleus**
- **Homogenous nucleation** is the easiest case: the formation a **solid nucleus** from a prior supersaturated **vapor**

### Questions:

- Under which conditions nuclei of films deposited are **thermodynamically stable**?
- What is the role of **surface energy** in film nucleation?
- How **large** nuclei are?
- What is the **energy barrier** to be surmounted in their formation?
- Which is the **growth mode** (island, planar, S-K)?
- How deposition rate and temperature **influence** nucleation energetics and size?

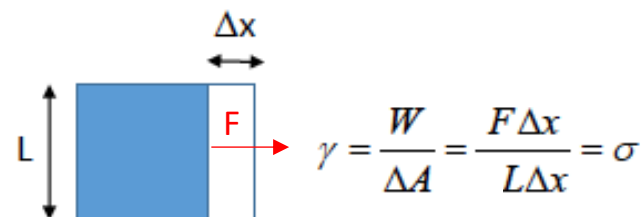


# Surface energies

## Capillarity (or droplet) theory of homogenous nucleation:

- A **solid (S)** nucleates from a prior instable **liquid (L)** or **vapor (V)** phase by establishing a S-L or S-V interface.
- **Interfacial (or surface) free energies  $\gamma$**  are associated to the interface (or surface).
- They quantify the *disruption of intermolecular bonds* that occur when a surface is created. Surfaces are *intrinsically less energetically favorable* than the bulk of a material (the molecules on the surface have more energy compared with the molecules in the bulk of the material), *otherwise there would be a driving force for surfaces to be created, removing the bulk of the material*. **The surface energy may therefore be defined as the excess energy at the surface of a material compared to the bulk, or the work required to build an area of a particular surface.**
- **Surface energy** is defined as  $\gamma = W/\Delta A$ , where  $W$  is the reversible work done on a material for increasing its surface area by  $\Delta A$ .
- **Surface tension ( $\sigma$ )** is defined as  $\sigma = F/L$  where  $F$  is the force counteracting the surface increase and  $L$  is the fixed side of the surface

Material	$\gamma$ (J/m <sup>2</sup> )
Glass	0.37
NaCl	0.40
Al	1.15
MgO	1.20
Si	1.24
Au	1.50
Cu	1.81
Ti	2.00
Ni	2.41
Fe	2.45
Pt	2.48
Co	2.53
Cr	3.32





# Homogeneous nucleation (1)

Homogeneous nucleation of a **spherical solid** phase of radius  $r$  from a supersaturated **vapor**:

- The gas-to-solid transformation modifies the chemical free energy of the system of  $\frac{4}{3}\pi r^3 \Delta G_V$ 
  - $\Delta G_V$  is the chemical free energy change per unit volume
  - For the **condensation reaction**  $V \rightarrow S$ ,  $\Delta G_V$  is given by  $\Delta G_V = -\frac{k_B T}{\Omega} \ln \frac{P_V}{P_S}$ , where  $P_S$  and  $P_V$  are the vapor pressure above the **solid** and of the **supersaturated vapor**, respectively, and  $\Omega$  is the atomic volume
  - $P_V > P_S$  for a **supersaturated** vapor (a supersaturated vapor of a compound is characterized by an higher partial pressure than the vapor pressure of the compound)  $\Rightarrow \Delta G_V < 0 \Rightarrow$  **nucleation takes place** because the free energy of the system reduces
- **Simultaneously, new surfaces or interfaces form  $\Rightarrow$  the surface free energy of the systems increases by  $4\pi r^2 \gamma$** , where  $\gamma$  is the S-V interfacial energy per unit area.
- The total free energy change in forming the nucleus is

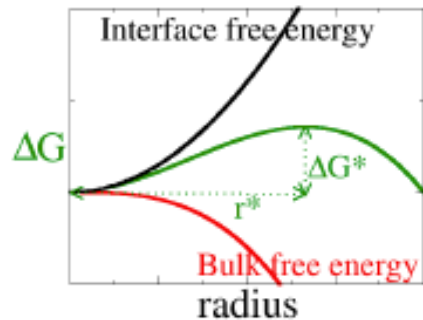
$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

## Homogeneous nucleation (2)

Homogeneous nucleation of a **spherical solid** phase of radius  $r$  from a supersaturated **vapor**:

Looking at the stationary point of  $\Delta G$  leads to the **equilibrium radius size**:

$$\Delta G = \underbrace{\frac{4}{3}\pi r^3 \Delta G_V}_{\text{Bulk } <0} + \underbrace{4\pi r^2 \gamma}_{\text{Surface/interface } >0} \Rightarrow \frac{d\Delta G}{dr} = 4\pi r^2 \Delta G_V + 8\pi r \gamma = 4\pi r (r \Delta G_V + 2\gamma) = 0 \Rightarrow \begin{cases} r^* = -\frac{2\gamma}{\Delta G_V} & (\Delta G_V < 0) \\ \Delta G^* = \Delta G(r^*) = \frac{16\pi\gamma^3}{3\Delta G_V^2} \end{cases}$$



$\Delta G^*$  represents the energy barrier to the nucleation process:

- If a spherical cluster with radius  $r < r^*$  forms by thermodynamical fluctuations, it is **unstable** and will **shrink** by losing atoms (reducing  $r$  for reducing  $\Delta G$ )
- Cluster with radius  $r > r^*$  have surmounted the nucleation energy barrier  $\Delta G^*$  and are **stable**. They tend to **further grow** (increasing  $r$  for reducing  $\Delta G$ )

## Homogeneous nucleation (3)

Homogeneous nucleation of a **spherical solid** phase of radius  $r$  from a supersaturated **vapor**:

**Nucleation rate:**  $\frac{dN}{dt} = N^* A^* \omega$ , with:

- $N^*$ =**equilibrium concentration (per cm<sup>3</sup>) of stable nuclei** (proportional to the Boltzmann factor) =  $n_s \exp(-\Delta G^*/k_B T)$ 
  - $n_s$ =density of all possible nucleation sites (nuclei/cm<sup>3</sup>),  $\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2}$
- $A^*$ =**critical area (cross section) for each nucleus** (cm<sup>2</sup>) =  $4\pi r^2$
- $\omega$  = **impingement atoms rate (atoms/cm<sup>2</sup>s)** =  $\alpha \frac{N_A (P_v - P_s)}{(2\pi MRT)^{1/2}}$ 
  - $\alpha$  = sticking coefficient (0-1)
  - $M$ =atomic weight

( $\phi = N_A P / (2\pi MRT)^{1/2}$  was the gas impingement flux in a chamber of pressure  $P$ , see Lecture #2)

$$\Rightarrow \frac{dN}{dt} = n_s \exp\left(-\frac{\Delta G^*}{k_B T}\right) 4\pi r^2 \frac{\alpha (P_v - P_s) N_A}{(2\pi MRT)^{1/2}}$$

**Note:** the nucleation rate is mostly influenced by the exponential term, that is function of  $\Delta G^*$  and thus of  $P_v/P_s$  (through  $\Delta G_v$ ):

$$P_v/P_s \text{ larger} \Rightarrow \Delta G_v^2 = \left(\frac{k_B T}{\Omega} \ln \frac{P_v}{P_s}\right)^2 \text{ larger} \Rightarrow \Delta G^*, r^* \text{ smaller} \Rightarrow \begin{cases} \text{nucleation is possible (smaller energy barrier and critical size)} \\ \text{the nucleation rate is larger} \end{cases}$$

# Capillarity theory of heterogeneous nucleation (1)

## Heterogeneous nucleation of a condensed film on a substrate:

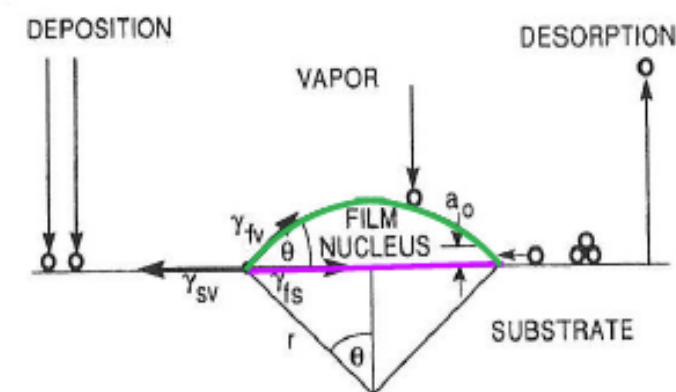
- We extend the capillarity theory of **homogeneous** nucleation (condensation from a vapor phase of a single chemical species – used only in some CVD processes) to a condensed film on a substrate → we have two species (substrate and depositing material) and two phases (the depositing material is both in solid – the film - and vapor phases)

➡ capillarity theory of **heterogeneous** nucleation

- Atoms or molecules in the **vapor** phase impinge on the **substrate** creating **nuclei** of mean dimension  $r$ .
- The **free-energy change** accompanying the formation of such nuclei is given by

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fV} + a_2 r^2 \gamma_{fS} - a_2 r^2 \gamma_{SV}$$

- $\Delta G_V$  is the chemical free energy change per unit volume that drives the condensation reaction (*as in homogenous nucleation*)
- $\gamma$  are the interfacial tensions between film (f), substrate (S) and vapor (V)
- $a_1 r^2$  is the curved surface area (interface f-V)
- $a_2 r^2$  is the projected area on the substrate (interface f-S)
- $a_3 r^3$  is the film volume



Schematic of basic nucleation processes on substrate during vapor deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

# Capillarity theory of heterogeneous nucleation (2)

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fV} + a_2 r^2 \gamma_{fS} - a_2 r^2 \gamma_{SV}$$

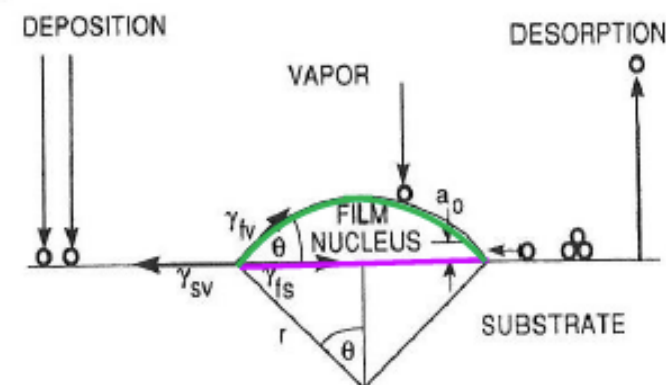
- $\Delta G_V$  is the chemical free energy change per unit volume
- $\gamma$  are the interfacial tensions between film (f), substrate (S) and vapor (V)
- $a_1 r^2$  is the curved surface area (interface f-V)
- $a_2 r^2$  is the projected area on the substrate (interface f-S)
- $a_3 r^3$  is the film volume

For the spherical cap-shaped solid nucleus in figure:

$$a_1 = 2\pi r^2 (1 - \cos \theta), a_2 = \pi r^2 \sin^2 \theta, a_3 = \pi r^3 (2 - 3 \cos \theta + \cos^3 \theta)$$

**Note:** when a new interface appears:

- the **surface energy of the film increases** (+ sign for the first two surface/interface terms, f-V and f-S)
- the **reduction of the S-V interface** under the cap implies a reduction in the system energy (- sign for the last interface terms, S-V)



Schematic of basic nucleation processes on substrate during vapor deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

**Mechanical equilibrium in the horizontal (parallel to substrate) direction:**

$$-\gamma_{SV} + \gamma_{fS} + \gamma_{fV} \cos \theta = 0$$

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{fS}}{\gamma_{fV}}$$

The wetting angle  $\theta$  depends **only on the material properties** (the interface tensions)

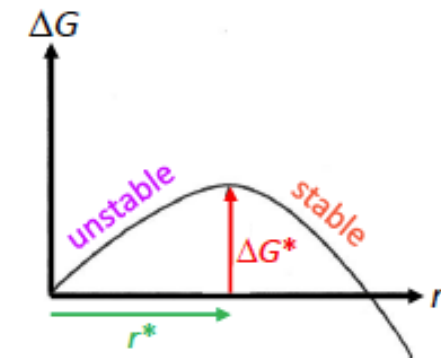
## Capillarity theory of heterogeneous nucleation (3)

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fV} + a_2 r^2 \gamma_{fS} - a_2 r^2 \gamma_{SV}$$

Looking at the stationary point of  $\Delta G$  leads to the **equilibrium radius size**:

$$\frac{d\Delta G}{dr} = 3a_3 r^2 \Delta G_V + 2a_1 r \gamma_{fV} + 2a_2 r \gamma_{fS} - 2a_2 r \gamma_{SV} = r \left( 3a_3 \Delta G_V r + 2(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV}) \right) = 0$$

$$\Rightarrow \begin{cases} r^* = -\frac{2(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV})}{3a_3 \Delta G_V} \\ \Delta G^* = \frac{4(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV})^3}{27a_3^2 \Delta G_V^2} \end{cases}$$



Heterogeneous nucleation behaves as homogeneous nucleation:

- $r^*$  is the **critical nucleus size** and  $\Delta G^*$  is the **critical free energy barrier** for nucleation.
- Nuclei are **unstable** for  $r < r^*$  (they disappear by shrinkig, lowering  $\Delta G$ ), and **stable** for  $r > r^*$  (they grow to supercritical dimensions by addition of atoms, lowering  $\Delta G$ )



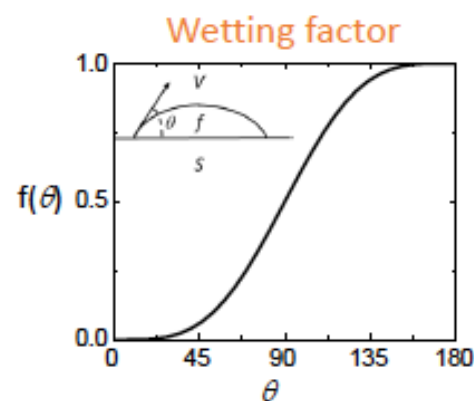
# Capillarity theory of heterogeneous nucleation (4)

For the spherical cap-shaped solid nucleus:

$$a_1=2\pi(1-\cos\theta), a_2=\pi\sin^2\theta, a_3=\pi/3 (2-3\cos\theta+\cos^3\theta)$$

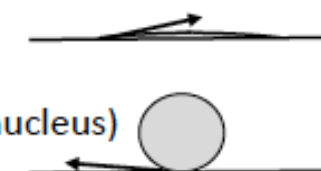
Using the mechanical equilibrium condition parallel to substrate ( $-\gamma_{SV} + \gamma_{FS} + \gamma_{FV} \cos\theta = 0$ ) we obtain:

$$\Delta G^* = \frac{4(2\pi(1-\cos\theta)\gamma_{FV} + \pi\sin^2\theta(\gamma_{FS} - \gamma_{SV}))^3}{3\pi^2(2-3\cos\theta+\cos^3\theta)^2 \Delta G_V^2} = \frac{4(2\pi(1-\cos\theta)\gamma_{FV} - \pi\sin^2\theta\gamma_{FV}\cos\theta)^3}{3\pi^2(2-3\cos\theta+\cos^3\theta)^2 \Delta G_V^2} = \underbrace{\frac{16\pi\gamma_{FV}^3}{3\Delta G_V^2}}_{\substack{\Delta G^* \text{ for} \\ \text{homogeneous} \\ \text{nucleation}}} \underbrace{\frac{2-3\cos\theta+\cos^3\theta}{4}}_{\substack{\text{Function of the} \\ \text{contact (wetting)} \\ \text{angle } f(\theta)}}$$



$\theta \rightarrow 0 \Rightarrow \Delta G^* \rightarrow 0$ : when the film **wets** the substrate, there is **no barrier** for nucleation

$\theta \rightarrow 180^\circ \Rightarrow \Delta G^* \rightarrow \Delta G^*$  for homogeneous nucleation (on a spherical nucleus)





# Capillarity theory of heterogeneous nucleation (5)

Other energy contributions (e.g. elastic strain) can be easily included in the free energy change expression:

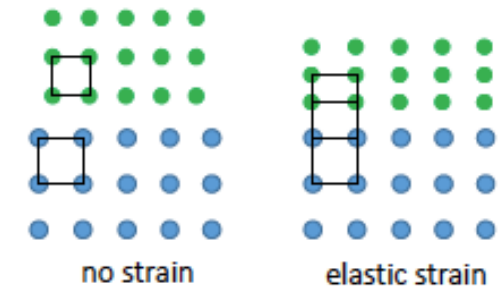
$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fV} + a_2 r^2 \gamma_{fS} - a_2 r^2 \gamma_{SV} + a_3 r^3 \Delta G_S$$

$\Delta G_S$  is the strain free-energy change per unit volume. It arises, e.g., from elastic strain of the film because of bonding mismatch between film and substrate.

$$\Rightarrow \Delta G^* = \frac{4(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV})^3}{27 a_3^2 (\Delta G_V + \Delta G_S)^2}$$

Note:

- $\Delta G_V < 0 \Rightarrow$  if  $\Delta G_S > 0$  (as in the figure) the energy barrier for nucleation  $\Delta G^*$  will increase
- However if  $\Delta G_S < 0$  (e.g. because of stress relief during nucleation on an *initially strained substrate*) the energy barrier for nucleation  $\Delta G^*$  will decrease and thus nucleation will be favoured
- $\Delta G^*$  could also be affected by substrate charge and impurities, affecting surface and/or volume electrostatic, chemical, etc., energy contributions  $\Rightarrow$  they can be treated in the same framework

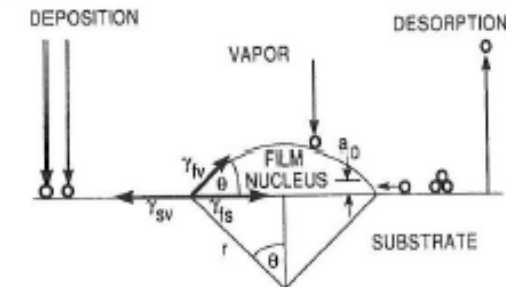


# Film growth modes (1)

Mechanical equilibrium in the horizontal (parallel to substrate) direction:

$$-\gamma_{SV} + \gamma_{FS} + \gamma_{fV} \cos \theta = 0 \quad (\text{Young's equation}) \Rightarrow \cos \theta = \frac{\gamma_{SV} - \gamma_{FS}}{\gamma_{fV}}$$

The wetting angle  $\theta$  depends **only on the material properties** (the interface tensions  $\gamma_{SV}$ ,  $\gamma_{FS}$ ,  $\gamma_{fV}$ )



Schematic of basic nucleation processes on substrate during vapor deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

- **Island growth:**  $\theta > 0 \Rightarrow \cos \theta = \frac{\gamma_{SV} - \gamma_{FS}}{\gamma_{fV}} < 1 \Rightarrow \gamma_{SV} - \gamma_{FS} < \gamma_{fV} \Rightarrow \boxed{\gamma_{SV} < \gamma_{FS} + \gamma_{fV}}$

Note: if we neglect  $\gamma_{FS}$ , island growth occurs when the surface tension of the film  $\gamma_{fV}$  exceeds that of the substrate  $\gamma_{SV}$   
 $\Rightarrow$  leaving the substrate uncovered leads to energy minimization

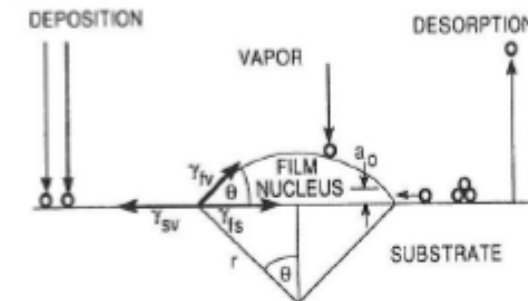
E.g.:  $\gamma_{fV} = 1.50 \text{ J/m}^2$  for Au,  $\gamma_{SV} = 0.86 \text{ J/m}^2$  for GaAs(110)  $\Rightarrow$  in general, deposited metals tend to cluster on semiconductor substrates

- **Layer growth:**  $\theta \approx 0 \Rightarrow \cos \theta = \frac{\gamma_{SV} - \gamma_{FS}}{\gamma_{fV}} = 1 \Rightarrow \gamma_{SV} - \gamma_{FS} = (\geq) \gamma_{fV} \Rightarrow \boxed{\gamma_{SV} \geq \gamma_{FS} + \gamma_{fV}}$

## Film growth modes (2)

- Island growth:  $\theta > 0 \Rightarrow \gamma_{SV} - \gamma_{FS} < \gamma_{FV} \Rightarrow \boxed{\gamma_{SV} < \gamma_{FS} + \gamma_{FV}}$

- Layer growth:  $\theta \approx 0 \Rightarrow \gamma_{SV} - \gamma_{FS} = (\geq) \gamma_{FV} \Rightarrow \boxed{\gamma_{SV} \geq \gamma_{FS} + \gamma_{FV}}$



Note#1: homo-epitaxy (or auto-epitaxy):  $\gamma_{FS} = 0$  (it is a special case of the layer growth condition in which the interface between film and substrate essentially vanishes)

Note#2: high-quality epitaxial growth of films requires **continuity during the growth** (no disruption to layer growth)  $\Rightarrow \gamma_{FS} = 0$   
because film (or overlayer to be grown) and substrate (or underlayer already grown) are the same

Note#3: consider a superlattice composed of alternating stacked **A** and **B** epitaxial films

- if the surface energies  $\gamma_{FV}$  and  $\gamma_{SV}$  are similar (e.g. for semiconductor-semiconductor) the superlattice can be **epitaxial** too (we assume to neglect  $\gamma_{FS}$ )
- if the surface energies  $\gamma_{FV}$  and  $\gamma_{SV}$  are different (e.g. for metal-metal or metal-semiconductor) epitaxy is *not guaranteed*
  - materials with low  $\gamma$  will wet substrates with large  $\gamma$  ( $\gamma_{FV} < \gamma_{SV}$ )
  - materials with large  $\gamma$  will clusterize on substrates with low  $\gamma$  ( $\gamma_{FV} > \gamma_{SV}$ )



# Morphological stability of strained layers (1)

How to address quantitatively strain at an interface between layers?

- From **elasticity theory** the **strain free energy** per unit volume ( $E_s$ ) can be expressed as

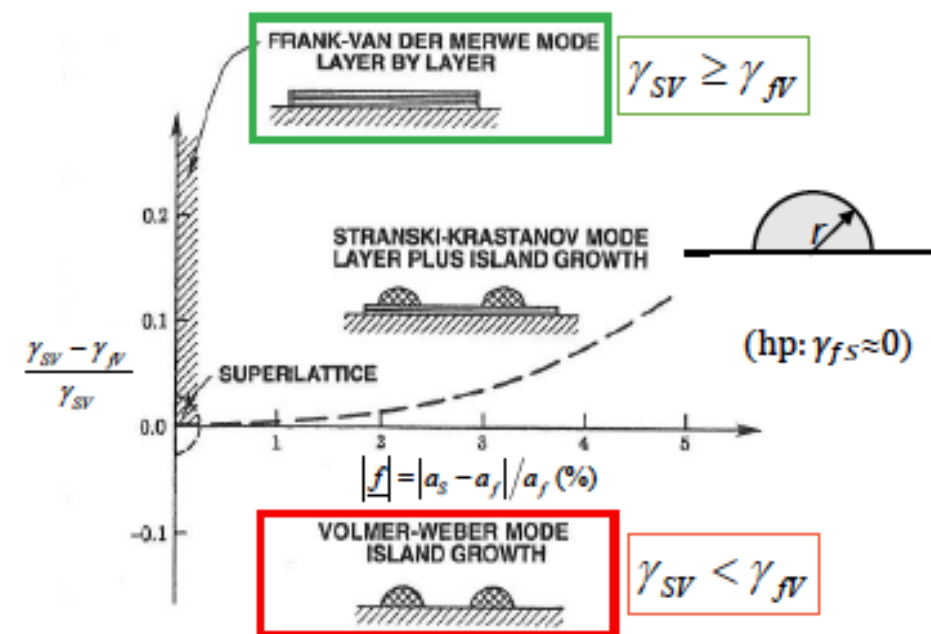
$$= \frac{1}{2} Y \varepsilon^2 h A$$

where  $Y$  is the elastic modulus of the film and  $\varepsilon$  is the strain.

- The strain  $\varepsilon$  at the interface can be measured as the **lattice mismatch strain** (or misfit) defined as

$$\underline{f} = \frac{a_s - a_f}{a_f}$$

where  $a_s$  and  $a_f$  are the lattice parameters of the upper layer (e.g., the film) and the lower layer (e.g., the substrate), respectively.



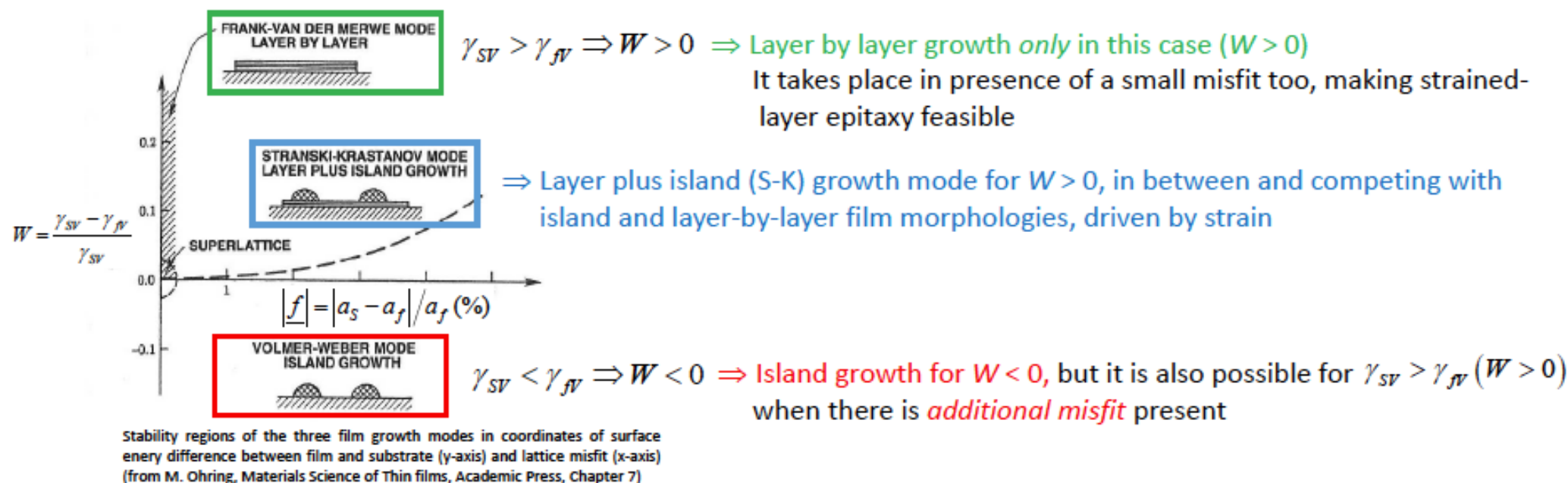
Stability regions of the three film growth modes in coordinates of surface energy difference between film and substrate (y-axis) and lattice misfit (x-axis) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

Which is the critical film thickness **beyond which a strained planar film roughens due to the growth of islands?**

$$h^* = \frac{2\gamma_{fs}}{Y(\varepsilon^2 - \underline{f}^2)}$$

- $\varepsilon$  is the mean misfit in the strained epilayer **after** nucleation, that minimizes the total energy by partially relaxing
- $\underline{f}$  is the misfit of the epilayer **prior** to nucleation, due to the misfit with the substrate

## Morphological stability of strained layers (5)



# Nucleation dependence on temperature

How substrate temperature and **deposition rate** influence the deposition process?

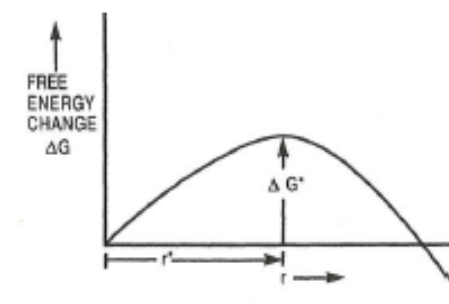
- Assuming an *inert substrate* (that is not reacting with the vapor phase) with  $\gamma_{fV} = \gamma_{fS}$  and  $\gamma_{VS} = 0$  we have (see slide 20):

$$r^* = -\frac{2(a_1\gamma_{fV} + a_2\gamma_{fS} - a_2\gamma_{SV})}{3a_3\Delta G_V} = -\frac{2(a_1 + a_2)\gamma_{fV}}{3a_3\Delta G_V}$$

$$\Rightarrow \left. \frac{\partial r^*}{\partial T} \right|_{\dot{R}} = -\frac{2}{3}(a_1 + a_2) \frac{\frac{\partial \gamma_{fV}}{\partial T} a_3 \Delta G_V - \gamma_{fV} a_3 \frac{\partial \Delta G_V}{\partial T}}{(a_3 \Delta G_V)^2} = \frac{2}{3}(a_1 + a_2) \frac{\gamma_{fV} \frac{\partial \Delta G_V}{\partial T} - \Delta G_V \frac{\partial \gamma_{fV}}{\partial T}}{a_3 (\Delta G_V)^2}$$

- Assuming typical values we have  $\left. \frac{\partial r^*}{\partial T} \right|_{\dot{R}} > 0$

- Moreover, we also have  $\left. \frac{\partial \Delta G^*}{\partial T} \right|_{\dot{R}} > 0$



Free energy change ( $\Delta G$ ) as a function of radius ( $r$ ). (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 1)



# Nucleation dependence on deposition rate

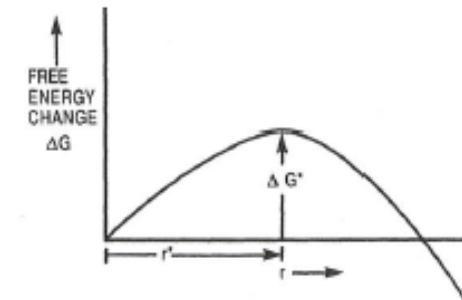
*How substrate temperature and deposition rate influence the deposition process?*

- $\Delta G_v$  is the chemical free energy change per unit volume (see slide 15)
- For the condensation reaction  $V \rightarrow S$ ,  $\Delta G_v$  is given by  $\Delta G_v = -\frac{k_B T}{\Omega} \ln \frac{P_v}{P_s}$ , where  $P_s$  and  $P_v$  are the vapor pressure above the solid and of the supersaturated vapor, respectively, and  $\Omega$  is the atomic volume
- Assuming the deposition rate  $\dot{R}$  (atoms/cm<sup>2</sup>s) on the film nucleus proportional to  $P_v$  and the equilibrium evaporation rate  $\dot{R}_e$  (from the film nucleus at the substrate temperature) proportional to  $P_s$ , we have  $\Delta G_v = -\frac{k_B T}{\Omega} \ln \frac{\dot{R}}{\dot{R}_e}$

$$\left. \frac{\partial r^*}{\partial \dot{R}} \right|_T = \left. \frac{\partial r^*}{\partial \Delta G_v} \right|_T \left. \frac{\partial \Delta G_v}{\partial \dot{R}} \right|_T = \frac{\partial \left[ -\frac{2(a_1 + a_2)\gamma_{sv}}{3a_3 \Delta G_v} \right]}{\partial \Delta G_v} \frac{\partial \left[ -\frac{k_B T}{\Omega} \ln \frac{\dot{R}}{\dot{R}_e} \right]}{\partial \dot{R}} = \frac{r^*}{\Delta G_v} \frac{k_B T}{\Omega \dot{R}}$$

- Because  $\Delta G_v < 0$ , we have  $\left. \frac{\partial r^*}{\partial \dot{R}} \right|_T < 0$

- Moreover, we also have  $\left. \frac{\partial \Delta G^*}{\partial \dot{R}} \right|_T < 0$



Free energy change ( $\Delta G$ ) as a function of radius ( $r$ ). (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 1)

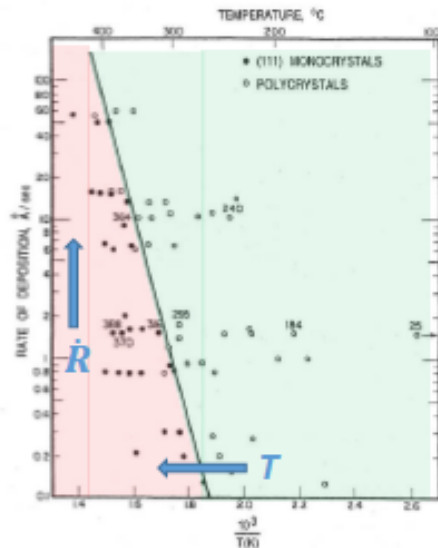


# Nucleation dependence on temperature and deposition rate

$\left. \frac{\partial r^*}{\partial T} \right _{\dot{R}} > 0$	$\left. \frac{\partial \Delta G^*}{\partial T} \right _{\dot{R}} > 0$
$\left. \frac{\partial r^*}{\partial \dot{R}} \right _T < 0$	$\left. \frac{\partial \Delta G^*}{\partial \dot{R}} \right _T < 0$

*Some observation on common effects observed in thin films deposition:*

- Higher  $T$  leads to higher critical radius  $r^* \Rightarrow$  an island structure persists to an higher coverage
- A nucleation barrier may exist at higher substrate  $T$ , while at lower  $T$  it is reduced in magnitude
- Because  $N^*$  (the equilibrium concentration of stable nuclei, see slide 17) exponentially depends on  $\Delta G^*$  ( $\propto \exp(-\Delta G^*/k_B T)$ ), the number of supercritical nuclei decreases rapidly with  $T \Rightarrow$  a continuous film will take longer to develop
- Increasing the deposition rate  $\dot{R}$  results in smaller islands (smaller  $r^*$ )
- Increasing the deposition rate  $\dot{R}$  also reduces the nucleation barrier (smaller  $\Delta G^*$ ), favouring continuous films at lower average film thickness



Dependence of microstructure on deposition rate  $\dot{R}$  and substrate temperature  $T$  for Cu films on NaCl(111) (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 1)

We associate:

- Large  $r^*$  and  $\Delta G^*$  to large crystallite or even **monocrystals**  $\Rightarrow$  favoured by **high  $T$**  and **low  $\dot{R}$**
- Small  $r^*$  and  $\Delta G^*$  to **polycrystalline** films  $\Rightarrow$  favoured by **low  $T$**  and **high  $\dot{R}$**

# Nucleation rate (1)

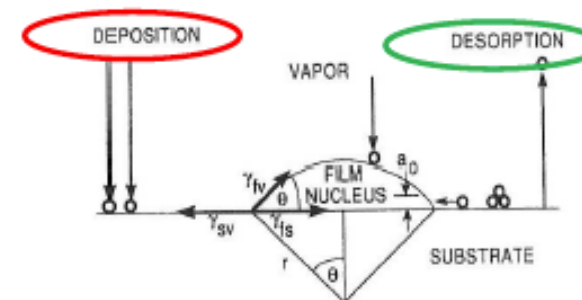
*How many nuclei of critical size form on the substrate per unit area and time?*

- The rate at which critical nuclei grow depends on the rate at which adsorbed monomers (adatoms) attach to it.
- Energetic vapor atoms which **impinge** on the substrate usually remain on the surface for a length time  $\tau_s$  before **desorbing**:

$$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{des}}{k_B T}\right)$$

where  $\nu$  is the vibrational frequency of an adatom on the surface ( $\sim 10^{13} \text{ s}^{-1}$ ) and  $E_{des}$  is the energy required to desorb it back into the vapor.

- Adatoms not yet accommodated to the substrate, executing random diffusive jumps, can form **stable pairs** with other adatoms or **attach** to larger atomic clusters or nuclei (it is unlikely that further return to the vapor phase)
- This typically happens at **substrate heterogeneities** (cleavage steps, edges, imperfections) where the binding energy of adatoms is larger than in a planar surface  $\Rightarrow$  the larger number of atomic bonds at this sites leads to **higher**  $E_{des}$ .

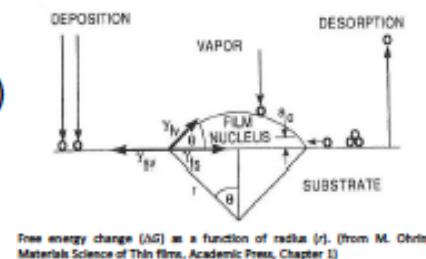


Schematic of basic nucleation processes on substrate during vapor deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

## Nucleation rate (2)

**Nucleation rate:**  $\frac{dN}{dt} = N^* A^* \omega$  (nuclei/cm<sup>2</sup>s) with:

- $N^*$ =equilibrium concentration (per cm<sup>2</sup>) of stable nuclei (proportional to the Boltzmann factor)
- $A^*$ =critical area (cross section) for each nucleus (cm<sup>2</sup>) =  $2\pi r^* a_0 \sin \theta$
- $\omega$  = impingement atoms rate (atoms/cm<sup>2</sup>s) onto nuclei with critical area  $A^*$



- Of the total nucleation site density, only  $n_a$  will be occupied by adatoms:  $n_a = \phi \tau_s = \frac{\tau_s N_A P}{(2\pi MRT)^{1/2}}$

$\phi = N_A P / (2\pi MRT)^{1/2}$  is the vapor impingement flux in a chamber of pressure  $P$ , see Lesson #2

$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{des}}{k_B T}\right)$  is the adatom lifetime on the substrate (between adsorption and desorption)

- Atoms that have not yet thermally accommodated to the substrate execute random diffusive jumps, ending up to accommodate in clusters or nuclei. After this accommodation, desorption becomes an unlikely process. The impingement rate onto area  $A^*$  thus considers **diffusive jumps** on the substrate, with a frequency given by

$\nu \exp\left(-\frac{E_s}{k_B T}\right)$ , where  $E_s$  is the activation energy for surface diffusion.

➡ The overall impingement flux is thus  $\omega = n_a \nu \exp\left(-\frac{E_s}{k_B T}\right) = \frac{\tau_s N_A P}{(2\pi MRT)^{1/2}} \nu \exp\left(-\frac{E_s}{k_B T}\right)$  (nuclei/cm<sup>2</sup>s)

## Nucleation rate (3)

Finally we obtain the **nucleation rate**:

$$\frac{dN}{dt} = N^* A^* \omega = n_s \exp\left(-\frac{\Delta G^*}{k_B T}\right) 2\pi r^* a_0 \sin \theta \frac{\frac{1}{\nu} \exp\left(\frac{E_{des}}{k_B T}\right) N_A P}{(2\pi MRT)^{1/2}} \nu \exp\left(-\frac{E_s}{k_B T}\right) =$$

Residence time prior to re-evaporation

Diffusion frequency on the substrate

$$= 2\pi r^* a_0 \sin \theta \frac{PN_A}{(2\pi MRT)^{1/2}} n_s \exp\left(\frac{E_{des} - E_s - \Delta G^*}{k_B T}\right)$$

Note:

- The nucleation rate exponentially depends on the nucleation energetics via  $\Delta G^*$  ( $\propto \exp(-\Delta G^*/k_B T)$ ) – that is **proportional to  $N^*$**  (the equilibrium concentration of stable nuclei)
- The nucleation rate is **proportional to the vapor pressure  $P$**
- The nucleation rate depends on  $T$  mainly via the exponential factor **POSITIVE OR NEGATIVE? TO CHECK** – the rate **decreases monotonically with  $T$**

# Cluster coalescence and depletion

*What happens to the density of stable nuclei in time?*

- First, it **increases** with time up to some maximum level...
- ... then it **decreases** because of coalescence phenomena.

*During growth and coalescence it typically happens that*

- the total projected area of nuclei on the substrate decreases
  - the height of the surviving clusters increases
- nuclei with defined crystallographic facets initially become rounded...
- ... whereas composite islands reassume a crystallographic shape with time
- when two islands with different crystal structure coalesce, the final composite island assumes the crystallographic orientation of the larger one
- the coalescence process appears to be liquid-like, with islands merging and changing shape following a liquid droplet motion model
- Before impacting and merging, cluster migrate over the substrate surface (cluster-mobility coalescence)

Coalescence mechanisms:

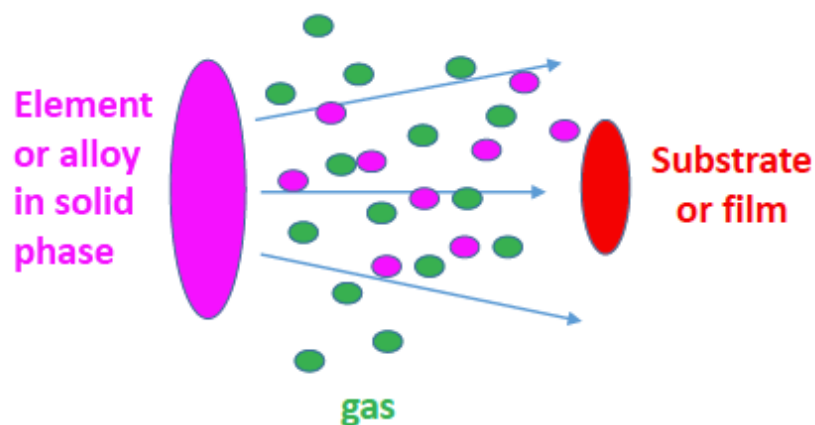
- Ostwald ripening
- Cluster migration
- Sintering

# Introduction to deposition techniques

Objective of **deposition** techniques:

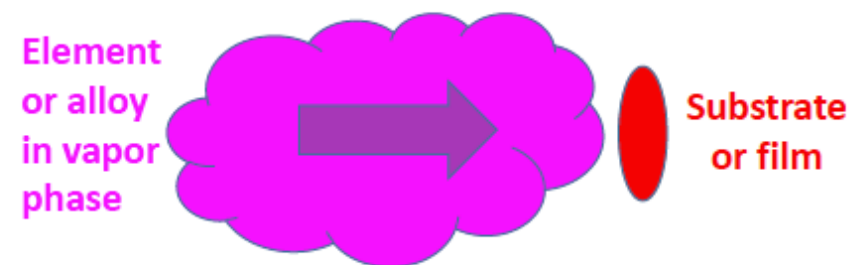
To controllably **transfer** atoms from a **source** to a **target**

*How the material is transferred from the **source** to the **target**?*



The **source** material is physically transferred from a condensed phase evaporant to the **target** substrate

**Physical vapor deposition (PVD)**



A **volatile** compound of the material to be deposited chemically reacts with other gases to produce a **nonvolatile** solid that deposits atomistically on the **target** substrate

**Chemical vapor deposition (CVD)**



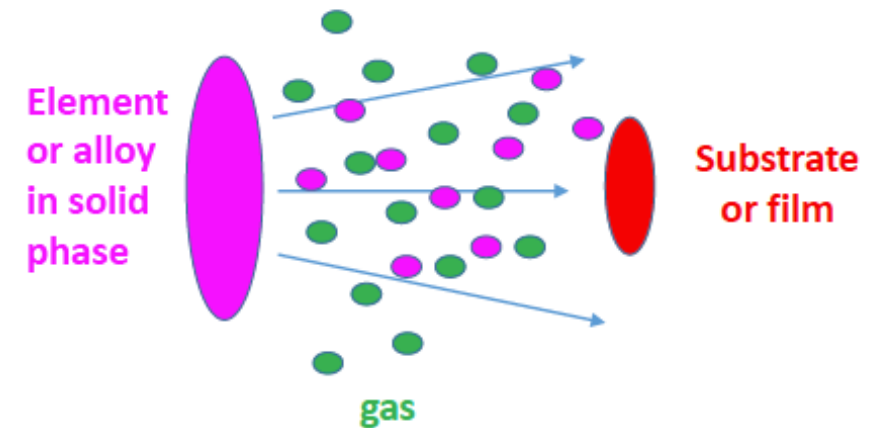
# Introduction to PVD techniques

*How the material is transferred from the **source** to the **target**?*

## Physically

The **source material** is physically transferred from a condensed phase evaporant to the **target substrate**

**Physical vapor deposition (PVD)**



*Which is the **physical mechanism** for transferring the material from the **source** to the **target**?*

➤ **evaporation** caused by absorption of **thermal** energy (liquid or solid targets) → *lecture 5*

*Which is the mechanism providing thermal energy to source atoms? Electrical heating, electron beam, pulsed laser,...*

➤ **sputtering** by **bombarding** solid surfaces with energetic **ions** → *lecture 6*

➤ In all cases the emitted atoms traverse a **high vacuum region** before to deposit on the target → *lecture 2*



# Evaporation rate

Hertz-Knudsen, 1882:

1. a liquid has a specific ability to evaporate at a given temperature;
2. the **evaporation rate** is *proportional* to the difference between the **equilibrium pressure of the evaporant** ( $P_e$ ) and the **hydrostatic pressure acting on it** ( $P_h$ )

➡ The **evaporation rate** from **liquid and solid sources** is given by  $\phi_e = \frac{\alpha_e N_A (P_e - P_h)}{(2\pi MRT)^{1/2}}$

where  $\phi_e$  is the **evaporation flux** (molecules/cm<sup>2</sup>s) and  $\alpha_e$  is the **coefficient of evaporation** (0-1).

Note: the other parameters ( $M, R, T$ ) and their dependences are equivalent to the gas impingement flux equation, see Lecture 2:  $\phi = N_A P / (2\pi MRT)^{1/2}$

The maximum **evaporation rate** is attained when  $\alpha_e=1$  and  $P_h=0$  (**high vacuum or UHV is needed**):  $\phi_e = \frac{N_A P_e}{(2\pi MRT)^{1/2}}$

$$\phi_e (\text{molecules/cm}^2\text{s}) = 3.513 \cdot 10^{22} \frac{P_e (\text{torr})}{(MT)^{1/2}}$$

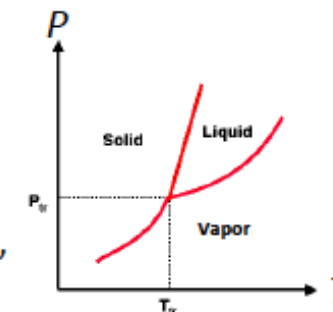
The **mass evaporation rate** instead is  $\Gamma_e (\text{g/cm}^2\text{s}) = \phi_e \frac{M}{N_A} = 5.84 \cdot 10^{-2} \left( \frac{M}{T} \right)^{1/2} P_e (\text{torr})$

Note: the evaporation rate **strongly depends on  $T$** , both through the  $T^{-1/2}$  dependence and because it deeply influences the **equilibrium pressure  $P_e$**

# Vapor pressure (1)

**Clausius-Clapeyron equation** for solid-vapor and liquid-vapor equilibria:  $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$

- $\Delta H$  and  $\Delta V$  refer to the difference between the **vapor** and the **condensed (solid or liquid)** phases, whereas  $T$  is the transition temperature (the two phases are in equilibrium and coexist)
- $\Delta V = V_{\text{vapor}} - V_{\text{condensed}} \approx V_{\text{vapor}}$  because typically  $V_{\text{vapor}} \gg V_{\text{condensed}}$
- Considering the vapor as a perfect gas, we have  $V_{\text{vapor}} = RT/P$  (for 1 mol)
- In general  $\Delta H = \Delta H(T)$ , but as a first approximation we assume  $\Delta H = \Delta H_e$ , the molar heat of evaporation

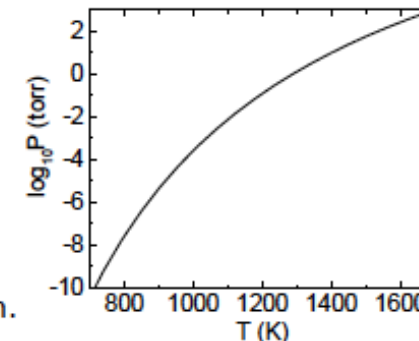


$$\Rightarrow \frac{dP}{dT} = \frac{P\Delta H_e}{RT^2}$$

$$\Rightarrow \frac{dP}{P} = \frac{\Delta H_e}{R} \frac{dT}{T^2} \Rightarrow \ln \frac{P}{P_0} = -\frac{\Delta H_e}{RT} \Rightarrow \ln P = -\frac{\Delta H_e}{RT} + \ln P_0$$

$$P(T) = P_0 \exp\left(-\frac{\Delta H_e}{RT}\right)$$

- $P_0$  is a constant that can be determined using the boiling point:  
 $\Delta H_e = \Delta H_v$  (the latent heat of vaporization),  $T$ =boiling temperature,  $P$ =1 atm.

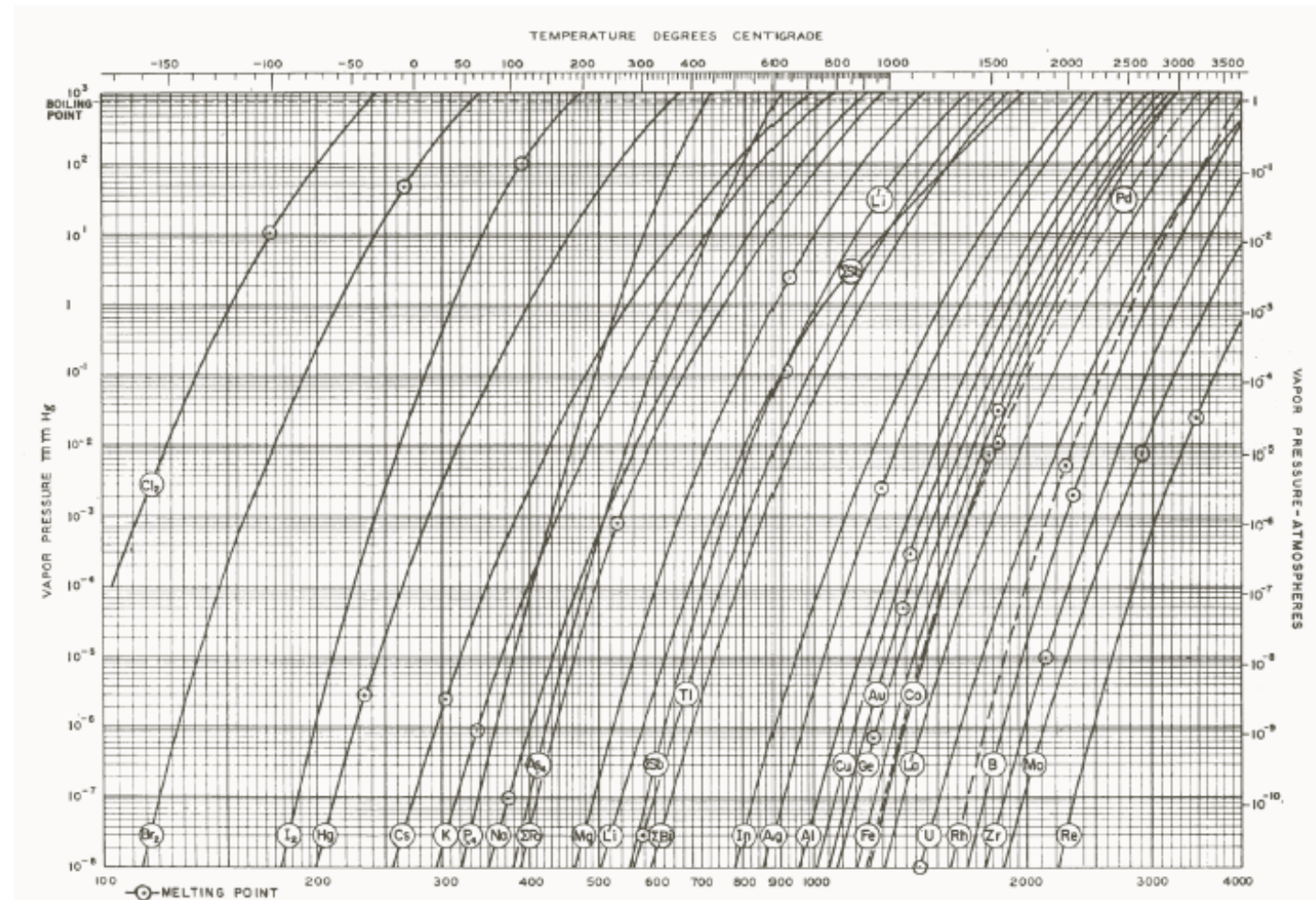


**Note:** this equation (**Arrhenius-type law**) holds for small temperature ranges, otherwise the  $\Delta H(T)$  dependence must be considered. E.g., for the vapor pressure of liquid a better approximation is

$$\log P \text{ (torr)} = -15.993/T + 12.409 - 0.999 \log T - 3.52 \cdot 10^{-6} T$$

## Vapor pressure (2)

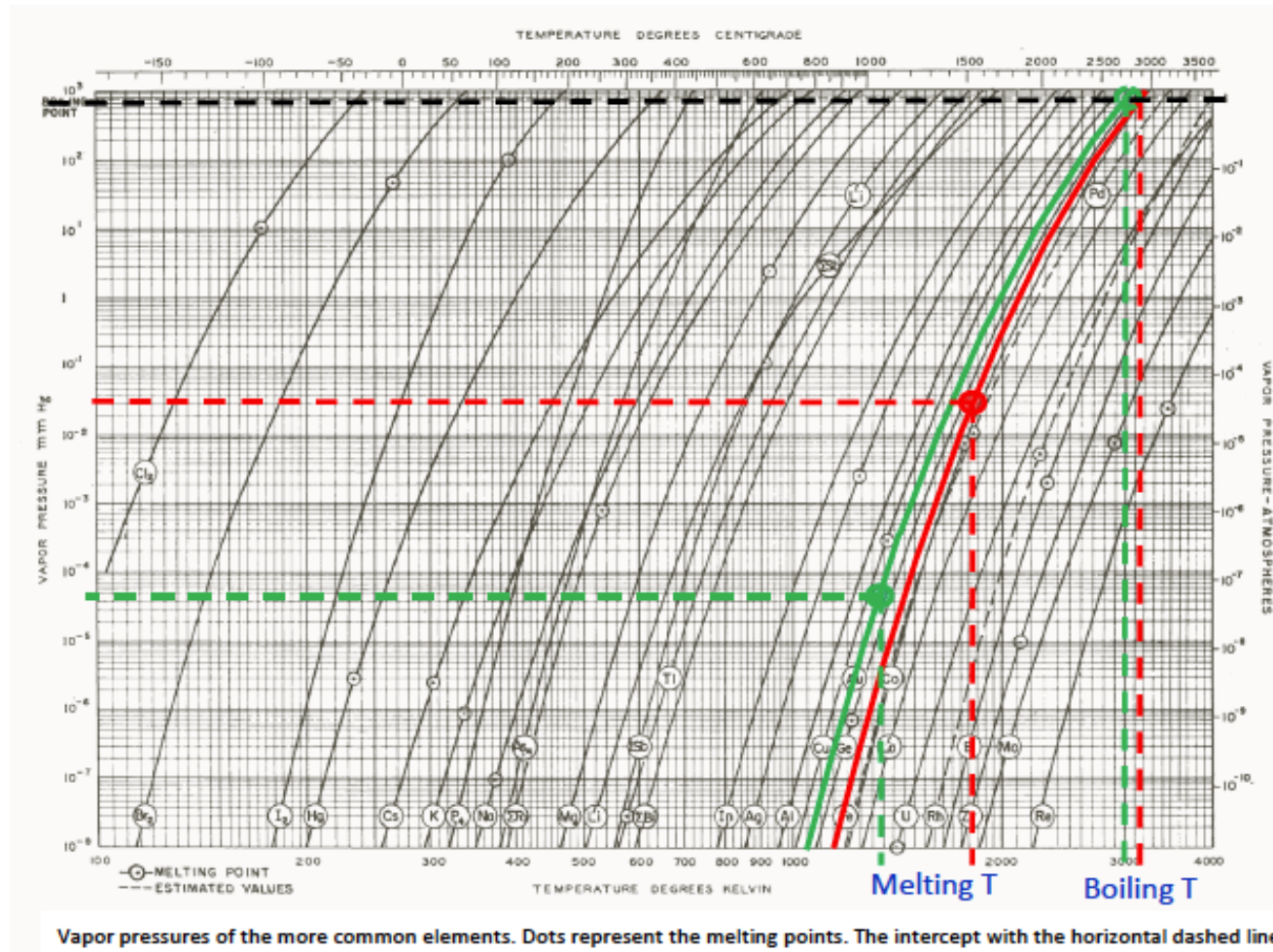
- **Experimental vapor pressures** (the pressure at which vapor and solid/liquid phases are in equilibrium and coexist) of the more common elements.
- Dots represent the melting points.
- The intercept with the horizontal dashed line correspond to the boiling points at ambient pressure.



(from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)



## Vapor pressure (3)



Vapor pressures of the more common elements. Dots represent the melting points. The intercept with the horizontal dashed line correspond to the boiling points, (from Lund Instrument Engineering - <https://www.powerstream.com/vapor-pressure.htm>)

Ex. **Fe**:  $T$  melting  $\approx 1850$  K @  $P \approx 3 \cdot 10^{-2}$  torr  
 $T$  boiling  $\approx 3100$  K @  $P = 1$  atm

Ex. **Au**:  $T$  melting  $\approx 1350$  K @  $P \approx 5 \cdot 10^{-5}$  torr  
 $T$  boiling  $\approx 3000$  K @  $P = 1$  atm

Element	Melting point (K)
Mg	920
Al	930
Si	1684
Cr	2177
Mn	1516
Fe	1808
Co	1765
Ni	1725
Cu	1355
Pd	1825
Ag	1232
Pt	2038
Au	1334

From oxford-vacuum.com

## Vapor pressure (4)

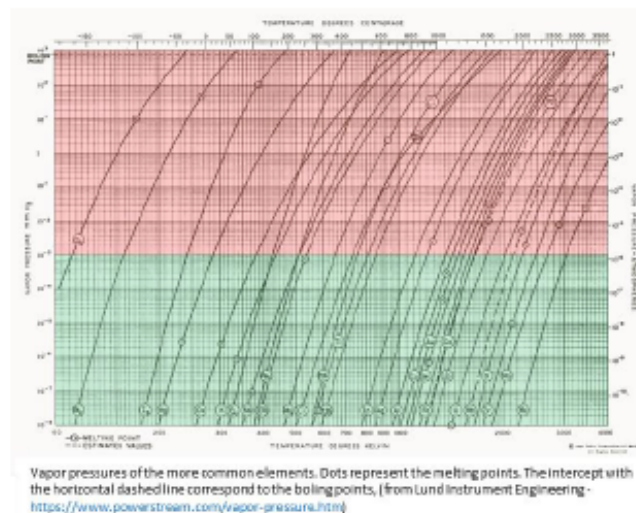
*Which is the criterion for discerning between evaporation from a solid or a liquid?*

*The vapor pressure needed to deposit with reasonably large rate ( $\Gamma_e$  and  $\phi_e$  are proportional to  $P_e$ ) effectively emanates from a solid or a liquid source?*

«Rule of thumb»: a **melt** will be required if the vapor pressure at the melting point is **lower** than about  $10^{-3}$  torr.

Ex. **Fe**: at the melting point  $P \approx 3 \cdot 10^{-2}$  torr  $\Rightarrow$  **no melting**  $\Rightarrow$  Fe **sublimes** from the **solid phase** (as well as Cr, Ti, Mo, Ni, Si, ...)

Ex. **Au**: at the melting point  $P \approx 5 \cdot 10^{-5}$  torr  $\Rightarrow$  **melting**  $\Rightarrow$  Au deposition is attained only when the source is **molten** (as well as Ge, Na, Cs, ..)



# Evaporation rate: example

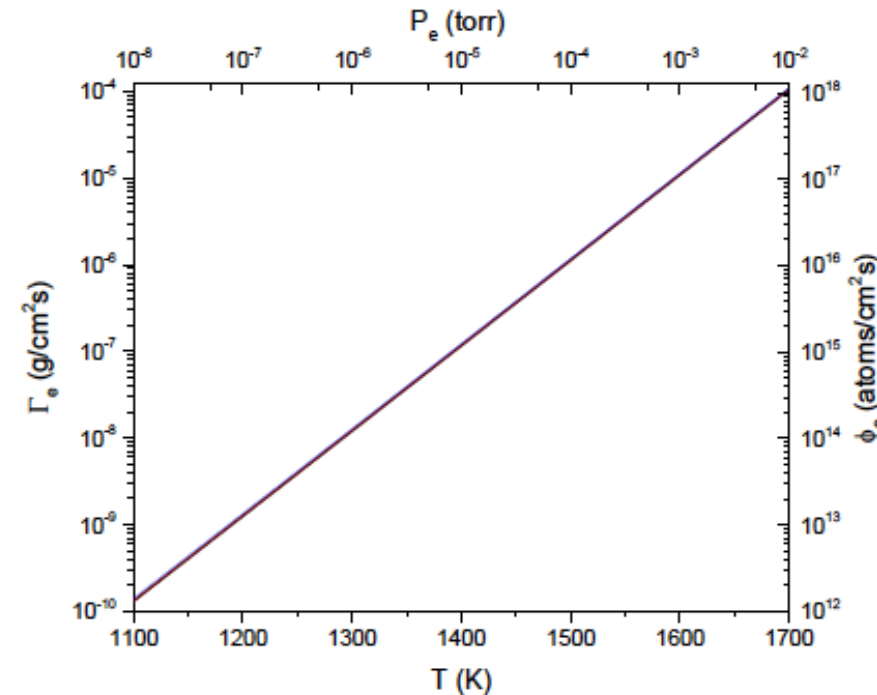
## Fe deposition by thermal evaporation

- from slide 10 we extract the  $P_e(T)$  curve
- we evaluate (using  $M=55.84$  g) the evaporation rates:

$$\Gamma_e (\text{g/cm}^2\text{s}) = \phi_e \frac{M}{N_A} = 5.84 \cdot 10^{-2} \left( \frac{M}{T} \right)^{1/2} P_e (\text{torr})$$

$$\phi_e (\text{atoms/cm}^2\text{s}) = 3.513 \cdot 10^{22} \frac{P_e (\text{torr})}{(MT)^{1/2}}$$

(note that the influence of the **temperature**  $T$  is mainly via  $P_e$  and not via the  $T^{-1/2}$  dependence)



*Which is the rate in terms of monolayer per second?*

- 1 ML corresponds to about  $10^{15}$  atoms/cm<sup>2</sup> (see lecture 2)  $\Rightarrow r(\text{ML} / \text{s}) = \frac{\phi_e (\text{atoms/cm}^2\text{s})}{10^{15} (\text{atoms/cm}^2)} = 3.513 \cdot 10^7 \frac{P_e (\text{torr})}{(MT)^{1/2}}$

*Which is the time needed for 1 ML coverage?*

- $t_{1\text{ML}} (\text{s}) = \frac{1}{r} = 2.85 \cdot 10^{-8} \frac{(MT)^{1/2}}{P_e (\text{torr})}$

$$\left[ \begin{array}{l} \text{Es.: } T=1400 \text{ K} \Rightarrow r=1.25 \text{ ML/s, } t_{1\text{ML}}=0.8 \text{ s} \\ T=1200 \text{ K} \Rightarrow r=0.014 \text{ ML/s}=0.84 \text{ ML/min, } t_{1\text{ML}}=73.7 \text{ s} \end{array} \right]$$

# Evaporation of multielement materials(1)

- **Metals**: they evaporate as atoms or clusters of atoms
- **Compounds**: the vapor composition is usually *different* from that of the liquid/solid source → stoichiometry is generally *not* preserved



both molecular association and **dissociation** can occur

Reaction type	Chemical reaction	Examples	Comments
Evaporation without dissociation	$MX(s,l) \rightarrow MX(v)$	SiO, GeO, MgO, CaF <sub>2</sub>	Compound stoichiometry is <b>maintained</b>
Evaporation with dissociation (g + g)			
a) Chalcogenides	$MX(s) \rightarrow M(g) + X(g)$	CdS, CdSe, CdTe	Deposited films are <b>metal-rich</b>
b) Oxides	$MO_2(s) \rightarrow MO(g) + 1/2 O_2(g)$	SiO <sub>2</sub> , GeO <sub>2</sub> , TiO <sub>2</sub>	<b>Separate sources</b> usually required
			Dioxides (and other complex oxides with larger oxidation number) are better deposited in <b>O<sub>2</sub> partial pressure</b> (reactive evaporation)
Decomposition (s/l + g)	$MX(s) \rightarrow M(s) + X(g)$ $MX(s) \rightarrow M(l) + X(g)$	III-V semiconductors (GaAs, InAs)	<b>Separate sources</b> required



## Evaporation of multielement materials(2)

*How to evaporate metal alloy films (e.g. Fe-Ni, Ni-Cr, Al-Cu) **preserving** the stoichiometry?*

- Atoms in **metallic alloys** are *less tightly bound* than in oxides  $\Rightarrow$  they tend to evaporate *separately* (as in III-V semiconductors)  $\Rightarrow$  they enter the vapor phase as *single atoms* (as if they were pure metals)
- We assume that the interaction energy between A and B atoms of an AB alloy is the same for any pair (AA, BB and AB)
- The Raoult law holds: 
$$\begin{cases} P_A = X_A P_{A0} \\ P_B = X_B P_{B0} \end{cases}$$

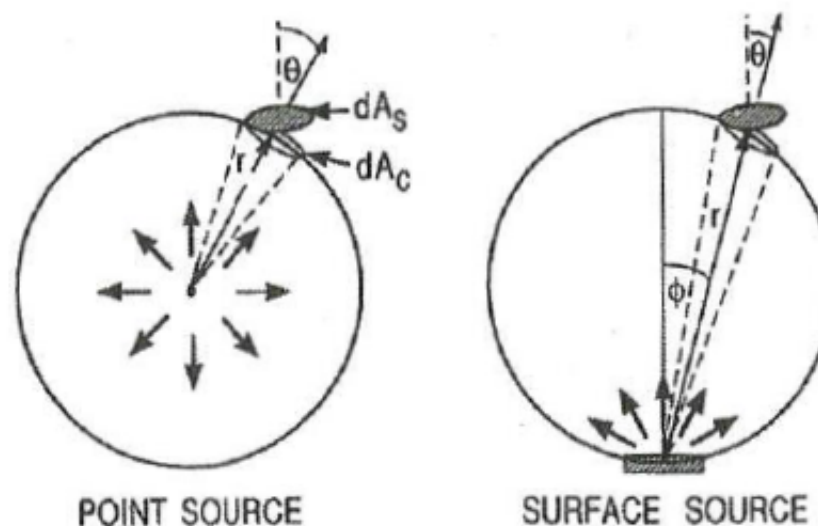
( $P_A$  is the **vapor pressure** of A in solution,  $P_{A0}$  is the vapor pressure of pure A,  $X_A$  is the **mole fraction** of A in the solution; the same for B;  $X_A + X_B = 1$ )

- In real situations, the mole fraction  $X$  must be replaced by the **activity  $a$**  that is the *effective* concentration of the material in the solution, taking into account the *different* evaporation rates from the solution (AB) or the pure materials (AA, BB).
- The *activity* can be related to the concentration by the activity coefficient  $\gamma$ :  $a = \gamma X \Rightarrow \begin{cases} P_A = \gamma_A X_A P_{A0} \\ P_B = \gamma_B X_B P_{B0} \end{cases}$
- Because the evaporation flux  $\phi_e$  is proportional to  $P_e / \sqrt{M}$  (see slide 7), at a fixed  $T$ , finally we have 
$$\frac{\phi_A}{\phi_B} = \frac{\gamma_A X_A P_{A0}}{\gamma_B X_B P_{B0}} \left( \frac{M_B}{M_A} \right)^{1/2}$$
 (with  $X_A + X_B = 1$ )
- However, during time the **source composition**, and that of the vapor by consequence, evolves (because of the loss of the more volatile component)  $\Rightarrow$  *if the fluxes are not compensated, a graded film of varying composition is deposited (disadvantage of evaporation methods!)*

# Deposition geometry (1)

*Which is the film uniformity that can be obtained by a given source?*

- Film uniformity depends on the source – substrate **geometry** (orientation, placement, distance, ...)
- The basic geometries are
  - **point source** – evaporant particles originate from an infinitesimally small region of a spherical source
  - **surface source** – evaporant particles originate from an extended area that can be considered a *superposition* of many point sources



Evaporation from a point source and a surface source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

## Deposition geometry (2)

- **Point source** – evaporant particles originate from an **infinitesimally small region** ( $dA_e$ ) of a **spherical (point) source** of surface area  $A_e$  with a **uniform mass evaporation rate**  $\Gamma_e$ ; the **substrate (S)** is at distance  $r$  from the point source

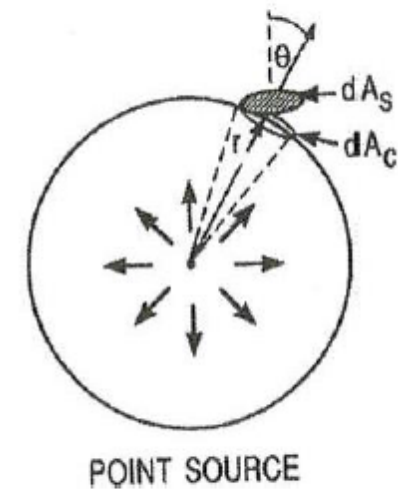
- The total **evaporated mass**  $M_e$  is given by  $M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt$
- The **mass**  $dM_s$  **deposited on the substrate** will fall on the portion of **substrate of area**  $dA_s$ , whose projected area on surface of a sphere of radius  $r$  is  $dA_c = dA_s \cos \theta$ , where  $\theta$  is the angle between the point source–substrate vector and the normal to the substrate surface.
- The following proportionality applies, assuming that the **total evaporated mass** is fully deposited on the sphere of area  $r$ :

$$\frac{dM_s}{dA_c} = \frac{M_e}{4\pi r^2}$$

$\Rightarrow$  the mass deposited per unit area finally is

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

- Note that deposition varies as
  - i)  $1/r^2$  (the source-substrate distance)
  - ii)  $\cos \theta$  (the geometric orientation of the substrate)



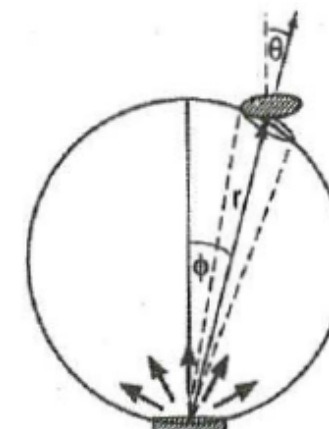
Evaporation from a point source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

## Deposition geometry (3)

- **Surface source** – it can be considered a superposition of point sources; their contribution to the vapor stream is **stronger** where the **evaporant emission angle**  $\phi$  (the angle between the surface source normal and the substrate) is **near zero**.

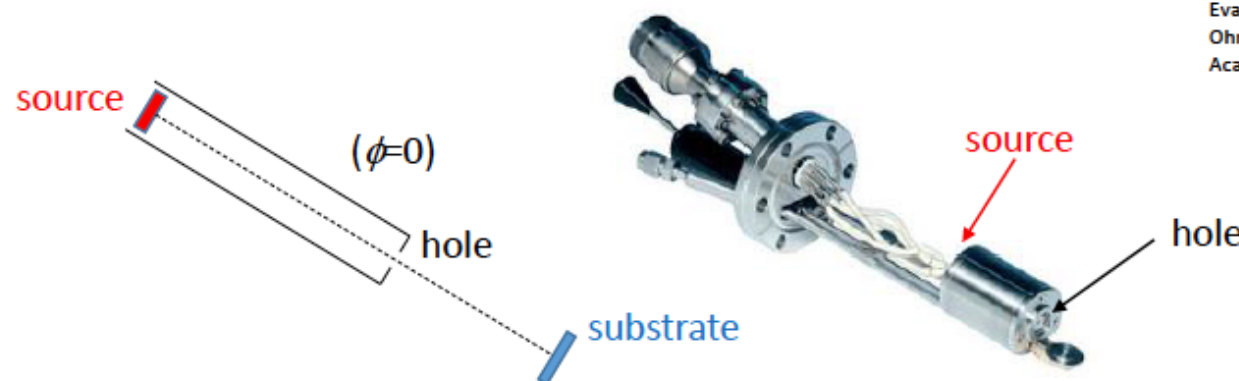
- The mass deposited per unit area is now dependent on angle  $\phi$ : 
$$\frac{dM_s}{dA_s} = \frac{M_e \cos \phi \cos \theta}{\pi r^2}$$
  
(Note that in the  $\phi=90^\circ$  direction there is no emission)

- **Knudsen cell source** – it makes use of an **isothermal enclosure** with a **small hole** through which the evaporant atoms or molecules will **diffuse**  $\Rightarrow$  it follows the same equation as above (with the cosine dependence on angle  $\phi$ )



**SURFACE SOURCE**

Evaporation from a surface source (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)



## Deposition geometry (4)

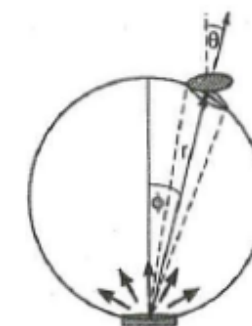
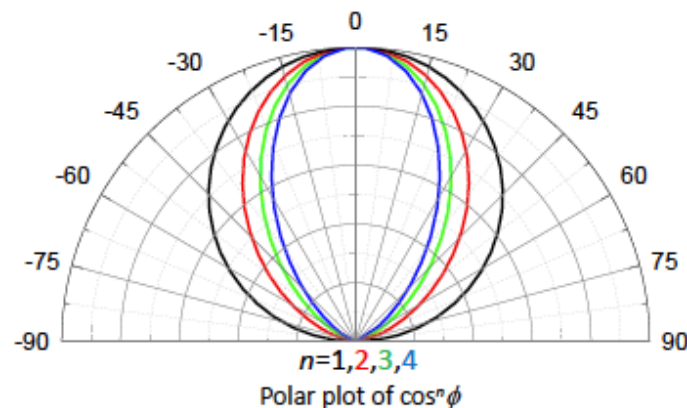
- Practically, the angular distribution of the **evaporant flux** depends on many parameters (as the evaporation crucible geometry)

→ a  $\cos^n \phi$  dependence has been experimentally found to be more appropriated

- $n$  determines the **shape** of the vapor cloud and the **angular distribution** (versus  $\phi$ ) of evaporant flux from the source
- $n$  scales as the ratio between the depth and the surface area of the molten source material  $\Rightarrow$  *narrower crucible have larger  $n$*  (they are used to *confine* the evaporated material to a *narrow angular spread*)

- The **mass deposited per unit area** is now 
$$\frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos \theta}{2\pi r^2}$$

Note: because of the **increased directionality** of the source, the **receiving surface area** scales down as  $\frac{2\pi r^2}{n+1}$



Evaporation from a surface source or Kunders cell (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)

# Film thickness uniformity (5)

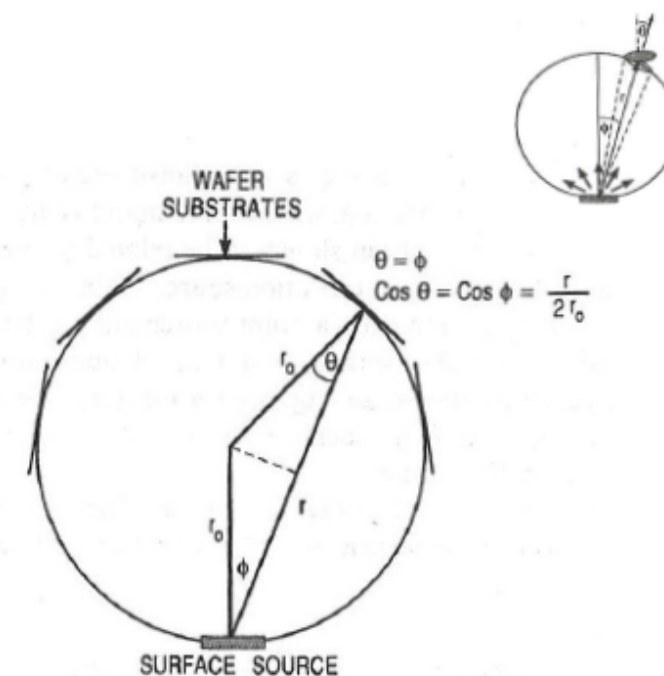
How to achieve maximum thickness uniformity on many substrates at the same time?

Both the surface sources and the substrates must be placed tangent to the surface of a sphere

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

Notes:

- the deposit thickness is **independent** on angle.
- This works with **surface sources** ( $n=1$ ), but *fails with more directional ones* ( $n>1$ )



Evaporation scheme to achieve uniform deposition (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 3)