

# Advanced Micro and Nanofabrication Technologies

Engineering Physics – Ingegneria Fisica - Cod. 055559

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## Lecture 3 Surfaces

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# Outline of the course

➤ **Where** we will grow? **Vacuum** ➡ **Vacuum technology: pressure, gas transport, vacuum systems**

➤ **On what** we will grow? **Surfaces** ➡ **Surface properties, nucleation, film growth modes**

➤ **Which kind** of films we will grow? **Epitaxy**

➤ **How** we will grow?

- **Physical techniques**
  - **Evaporation**
  - **Sputtering**
- **Chemical techniques**

➤ **How** we will check the growth? **Characterization**

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

# Why surfaces are important?

## How growth takes place?

Condensation of atomic clusters on the substrate

↓

Formation of a continuous film

↓

Film thickening due to additional deposition on top of the deposited film

↓

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

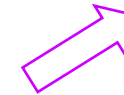


Relationships between growth process and film structure

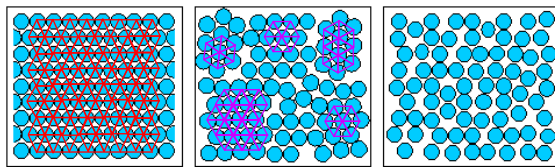


Understanding properties of the deposited films

Microscopic (atomistic) view



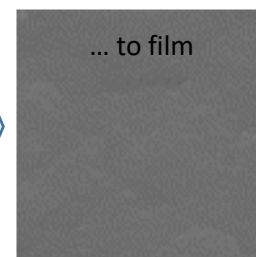
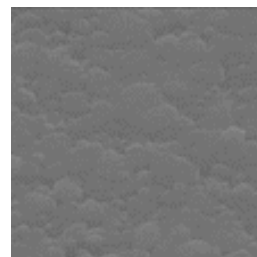
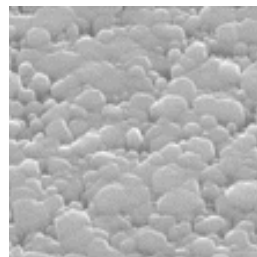
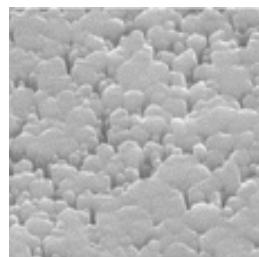
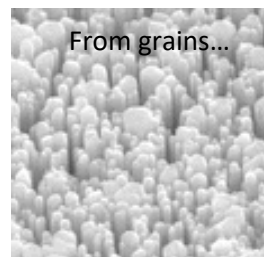
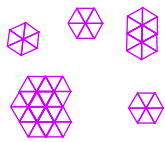
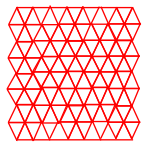
Macroscopic (thermodynamic) view



Single crystal  
Periodic across the whole volume.

Polycrystal  
Periodic across each grain.

Amorphous solid  
Not periodic.

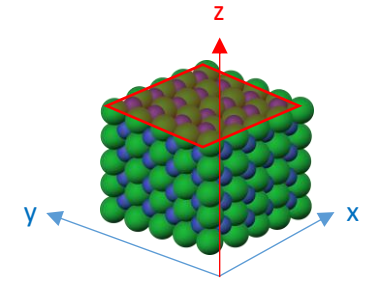


Es. ZnO on sapphire ( $\text{Al}_2\text{O}_3$ )

# What happens on surfaces?

- Electronics properties
- Structural properties

} **Different** from bulk because of **broken** translational symmetry!

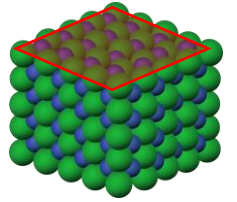


the crystal is **infinite** along x and y, but **finite** along z → a **surface** is created with properties different from bulk

- Adsorption effects → *How the surface adsorption and desorption energies of atoms depositing on the surface influence surface coverage?*

NOTE: this description is based on an **atomistic** description of the surface → **microscopic** view

# Structural properties



Hp: clean surface (no contamination by adsorbed gases and compounds) → atomically sharp interfacial demarcation between condensed-phase and gas-phase atoms

- Minimization of the overall electronic and bonding energies in the topmost atomic layers makes the surface crystallography **different** from that of the bulk.

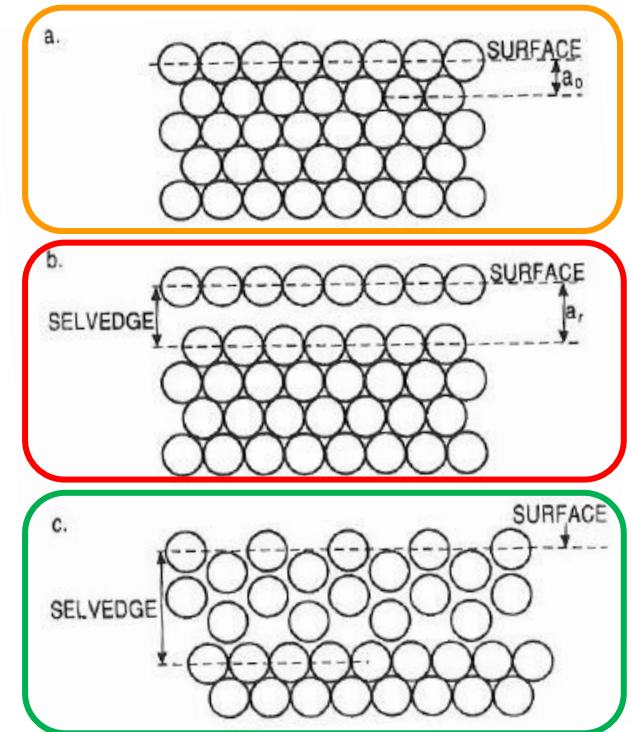
a) Bulk-like condition ⇒ *not likely* because of the loss of vertical symmetry leaving exposed bonds

b) Atomic relaxation outward ⇒ **likely** if the absence of some bonding forces results in new equilibrium positions.

The symmetry *parallel* to the surface is **preserved**, but not the symmetry normal to the surface.

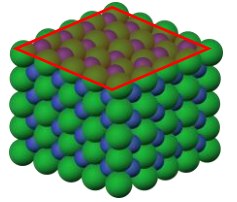
c) Reconstructed layer ⇒ **possible** because surface atoms rearrange to minimize energy in a structure with *different symmetry* than bulk.

Many surface properties (chemical, electrical, optical, ...) can change.



Schematic cross-sectional views of close-packed atomic positions at a solid surface: (a) Bulk exposed plan; (b) Atomic relaxation outward; (c) Reconstruction of outer layers (from M. Ohring, Materials Science of Thin films, Academic Press, Chapter 7)

# Electronics properties

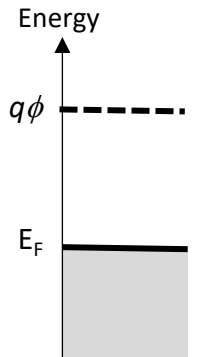


Hp: clean surface (no contamination by adsorbed gases and compounds)  $\Rightarrow$  atomically sharp interfacial demarcation between condensed-phase and gas-phase atoms

- Near the surface the **periodicity** of the wave function in the bulk is **broken**  $\Rightarrow$  **new electronic effects arise**

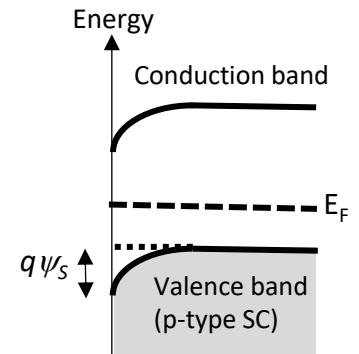
## Metals:

- Surface states appear as predicted by the Schrödinger equation solutions for electrons in terminated periodic lattices
- The difference in the electron potential between surface states and bulk states is the **Work Function ( $\phi$ )**
- $q\phi$  is the **energy barrier** that electrons with Fermi energy in the bulk must surmount for leaving the solid ( $q\phi \sim 2-5$  eV), avoiding to be trapped by surface states



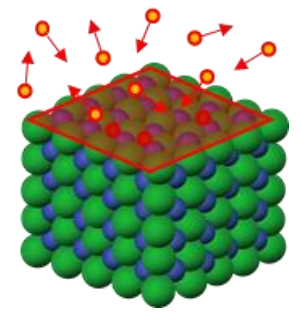
## Semiconductors:

- Surface states** are generated by the **severed covalent bonds** at the semiconductor surface
- When an **electron or hole** occupies a surface state, **electrostatic fields** originated from it penetrate the valence band (VB) and produce a variation of potential, that manifests as a **band bending**
- A nonzero **electrical potential**  $\psi_s$  exists at the surface due to **band bending**



# 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. It is an **exothermic** reaction.



## **Physisorption** (*physical* adsorption)

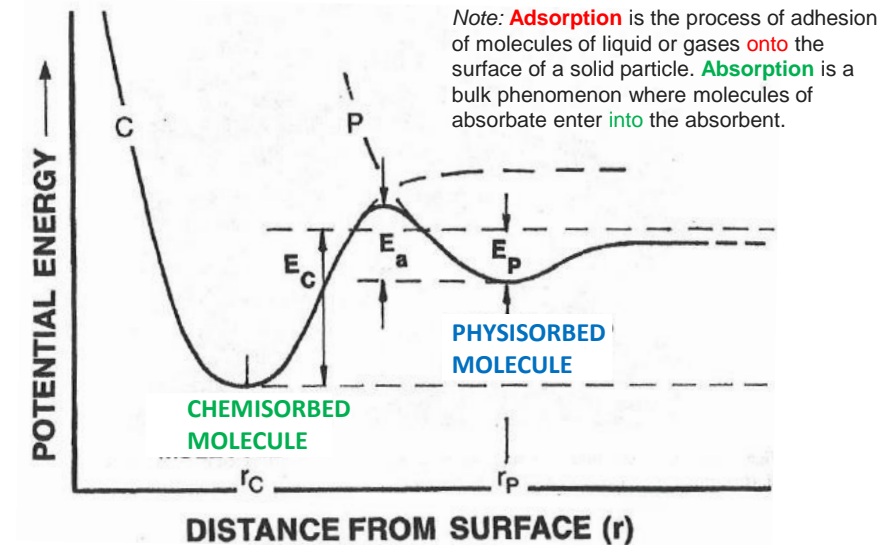
the particle is stretched or bent, but **retains its identity**; **van der Waals** forces bond it to the surface

## **Chemisorption** (*chemical* adsorption)

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

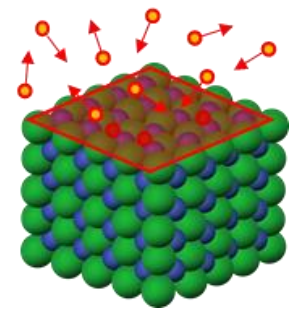
In the following we will use

- composite energy of adsorption** (integrated over all adsorption states)  $E_{ads} (<0)$
- composite energy of desorption** (integrated over all desorption states)  $E_{des} (>0)$



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)

# Adsorption effects (1)



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

- Consider a vapor phase containing adatoms at partial pressure  $P$ , that will condensate on a substrate surface

(Note: in the following, for simplicity we will call «substrate» the underlayer on which the film will be grown, either a true substrate or a film previously deposited, satisfying the hypothesis of cleanliness and sharpness)

- The net time rate of the substrate coverage  $\theta$  is given by:

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

(Note:  $k_{ads}$  and  $k_{des}$  do not have the same dimension)

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  $k_{ads}$ , that depends on the composite adsorption energy as:

$$k_{ads} \sim \exp\left(-\frac{E_{ads}}{k_B T}\right) \Rightarrow k_{ads} \text{ increases when } |E_{ads}| \text{ increases } (E_{ads} < 0 \text{ because adsorption is always exothermic})$$

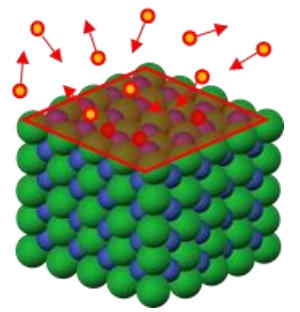
- The second term is the rate of adatoms desorption from the occupied surface sites ( $\theta$ ); it is proportional to the desorption rate  $k_{des}$ , that depends on the composite desorption energy as:

$$k_{des} \sim \exp\left(-\frac{E_{des}}{k_B T}\right) \Rightarrow k_{des} \text{ decreases when } E_{des} \text{ increases } (E_{des} > 0 \text{ because desorption is always endothermic})$$



# Adsorption effects (2)

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

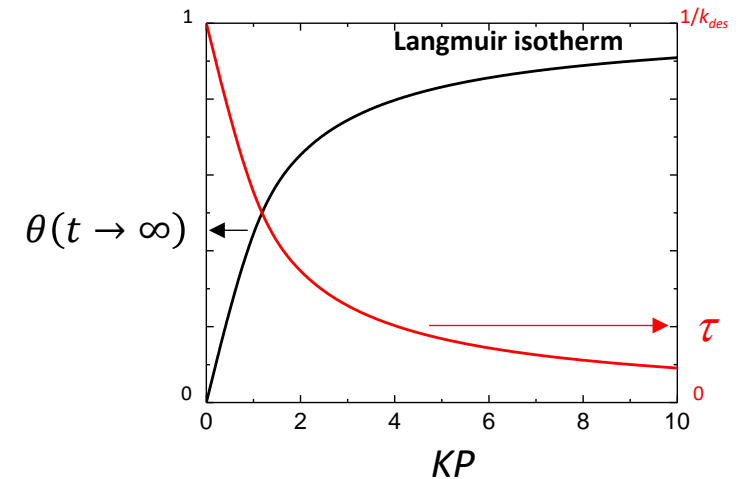


$$\frac{d\theta}{dt} = k_{ads}P(1 - \theta) - k_{des}\theta \quad \Rightarrow \quad \text{The solution is: } \theta(t) = \frac{KP}{1 + KP} [1 - \exp(-k_{des}(1 + KP)t)], \text{ with } K = \frac{k_{ads}}{k_{des}}$$

$$\text{We define the time constant } \tau = [k_{des}(1 + KP)]^{-1} \quad \Rightarrow \quad \theta(t) = \frac{KP}{1 + KP} [1 - \exp(-t/\tau)]$$

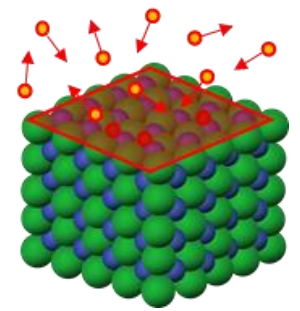
Note that:

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



Note:  $KP = \frac{k_{ads}}{k_{des}}P \gg 1$  means large  $P$  and/or large  $k_{ads}$  and/or small  $k_{des}$ , i.e. large  $|E_{ads}|$  and/or large  $E_{des}$

# What «pressure» does mean?



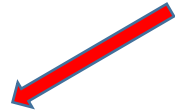
$$\frac{d\theta}{dt} = k_{ads}P(1 - \theta) - k_{des}\theta$$

$$\theta(t \rightarrow \infty) \approx \frac{KP}{1 + KP}$$

$$\tau = [k_{des}(1 + KP)]^{-1}$$



- The **pressure**  $P$  which physical quantity does represent in a **deposition process**?



## Evaporant material

Originating from a **source**  
To be **deposited** on the surface



**Local** pressure (close to surface)

**P** determines the surface  
coverage, morphology, growth  
rate, ...



## Residual gases

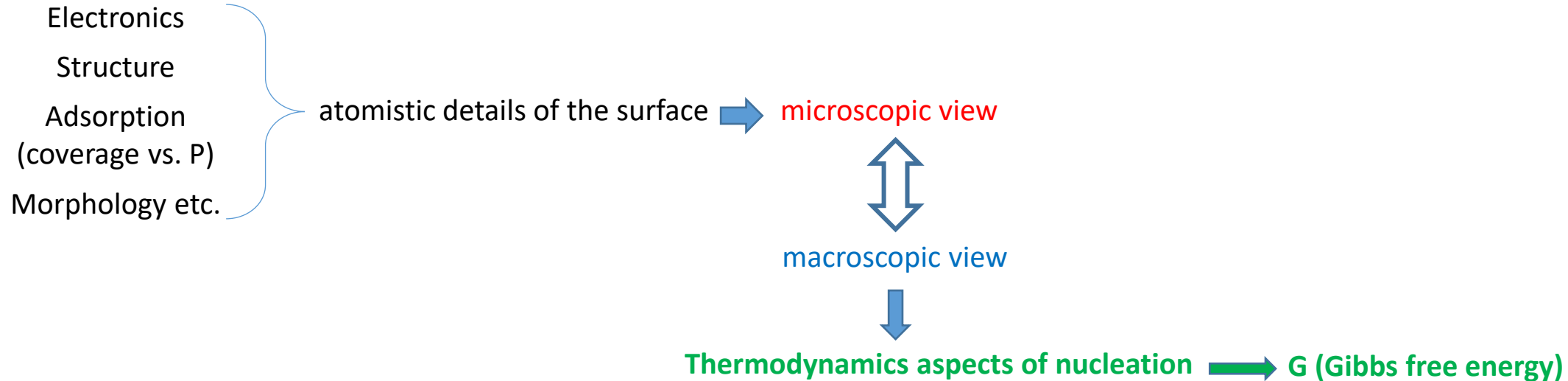
Originating from **degassing**, bad pumping etc.  
NOT to be **deposited** on the surface



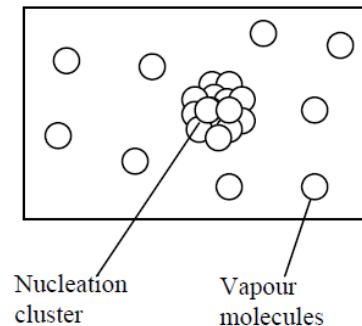
**Global** pressure (everywhere in the chamber)

**P** of residual gases as low as  
possible ( $\ll$  **P** evaporant material)

# From micro to macroscopic view



- **Nucleation** involves the creation a **new phase**, with generally **different** structure and/or composition (e.g. a solid phase), **from a previously stable phase** (e.g. a vapor phase) when critical boundaries between stable phases 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 of a **solid nucleus** from a prior supersaturated **vapor**.



## Questions:

- Under which conditions nuclei of deposited films 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)?
- Which is the effect of **strain** in volume or at interfaces?

# Thermodynamics

- **Surface energy** associated to surface or interface creation

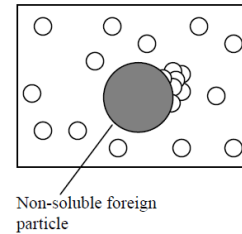
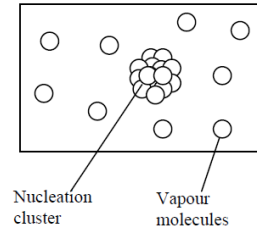


- **Homogeneous nucleation** → *same material*

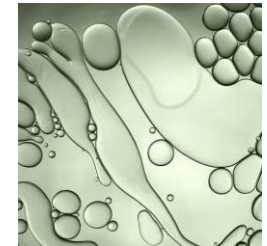


- **Heteogeneous nucleation** → *different materials*

Growth of a film on a  
different substrate



**Capillarity (or droplet) theory** – solid nucleates  
from liquid or vapor phase



- **Film growth modes** → *islands* vs. *layer by layer*
  - **Strained layers** morphological stability → *layer plus islands*

Note: this description is based on a **thermodynamic** description of the nucleation process → **macroscopic** view

# Surface energies

## Capillarity (or droplet) theory of homogeneous 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 material from the bulk.*

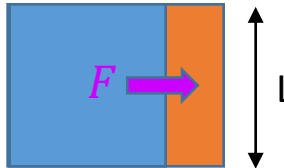
Material	$\gamma$ (J/m <sup>2</sup> )
Glass	0.37
NaCl	0.40
Al	1.15
MgO	1.20
Si	1.24
Au	1.50
Cu	1.81
Ti	2.00
Ni	2.41
Fe	2.45
Pt	2.48
Co	2.53
Cr	3.32

- **The surface energy may be defined as the **excess energy at the surface of a material compared to the bulk** :**

$\gamma = W / \Delta A$ , where W is the reversible work done on a material for increasing its surface area by  $\Delta A$

$$\gamma = \frac{W}{\Delta A} = \frac{F \Delta x}{2L \Delta x}$$

Note: the factor 2 appears because the surface has two sides, bottom and top.



- **The surface tension may be defined as the **force required to move the side of a particular surface** :**

$\sigma = F / 2L$ , where F is the force counteracting the surface increase and L is the fixed side of the surface

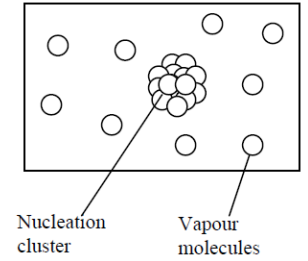
$$\sigma = \frac{F}{2L}$$

### Notes:

- These formulas apply to a liquid → in this case  $\gamma = \sigma$
- They are *not* strictly true for a solid because the work to displace molecules inside the solid – that was zero for a fluid – must be taken into account

# Homogeneous nucleation (1)

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



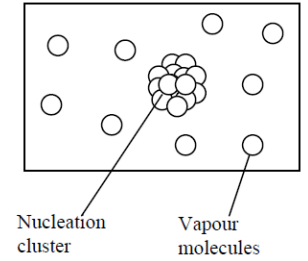
*Note:* It represents «rare» processes, but it is easy to model because it considers a single chemical species.

It does *not* consider film growth on a substrate, but nucleation of spheric particles with radius  $r$ .

- We assume that the vapor of the compound to be deposited is in a supersaturation condition, i.e. it is characterized by a higher partial pressure ( $P_V$ ) than the vapor pressure of the compound ( $P_S$ ):  $P_V > P_S$   
[The vapor pressure is the pressure, at a given temperature, at which vapor and condensed (solid) phases of the compound are in equilibrium and coexist]
- This situation can be achieved i.e. by reducing the volume and/or increasing the pressure in the deposition chamber, where the compound is contained, to achieve the condition  $P_V > P_S$ .
- The vapor-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 during the vapor (V→S) phase transition
  - $\frac{4}{3}\pi r^3$  is the volume of the spherical nucleus of radius  $r$  nucleated from the vapor phase
  - For the condensation reaction V→S,  $\Delta G_V$  is given by  $\Delta G_V = -\frac{k_B T}{\Omega} \ln \frac{P_V}{P_S}$ , where  $T$  is the temperature above the nucleus (at which  $P_S$  is evaluated) and  $\Omega$  is the atomic volume
  - $P_V > P_S$  for a supersaturated vapor  $\Rightarrow \Delta G_V < 0 \Rightarrow$  nucleation reduces the free energy of the system

# Homogeneous nucleation (2)

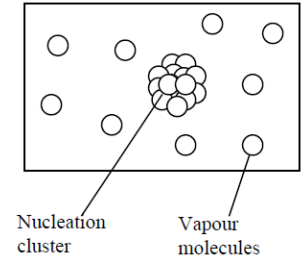
Homogeneous nucleation of a spherical solid phase of radius  $r$  from a supersaturated vapor



- The gas-to-solid transformation modifies the chemical free energy of the system of  $\frac{4}{3}\pi r^3 \Delta G_V$ 
  - $\Delta G_V < 0$  is the chemical free energy change per unit volume  $\Rightarrow$  the nucleation decreases the chemical free energy of the system
- Simultaneously, new surfaces or interfaces form  $\Rightarrow$  the surface free energy of the systems increases by  $4\pi r^2 \gamma$ , where  $\gamma > 0$  is the S-V interfacial energy per unit area
- The **total Gibbs free energy change** in forming the nucleus is then 
$$\Delta G = \underbrace{\frac{4}{3}\pi r^3 \Delta G_V}_{\text{Bulk } < 0} + \underbrace{4\pi r^2 \gamma}_{\text{Surface/ interface } > 0}$$
  - *In which conditions the process of nucleation becomes spontaneous ( $\Delta G < 0$ )?*
    - *In which conditions a nucleus is in equilibrium ( $\Delta G = 0$ )?*

# Homogeneous nucleation (3)

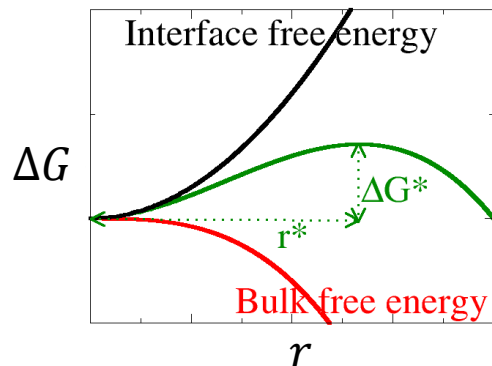
Homogeneous nucleation of a spherical solid phase of radius  $r$  from a supersaturated vapor



Looking at the stationary point of  $\Delta G$  leads to the equilibrium radius size  $r^*$  and energy barrier  $\Delta G^*$ :

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma \quad \Rightarrow \quad \frac{d\Delta G}{dr} = 4\pi r^2 \Delta G_V + 8\pi r \gamma = 4\pi r (r \Delta G_V + 2\gamma) = 0 \quad \Rightarrow \quad \begin{cases} r^* = -\frac{2\gamma}{\Delta G_V} & (\Delta G_V < 0) \\ \Delta G^* = \Delta G(r^*) = \frac{16\pi\gamma^3}{3\Delta G_V^2} \end{cases}$$

- Which is the physical meaning of the energy barrier  $\Delta G^*$  and the equilibrium radius size  $r^*$ ?

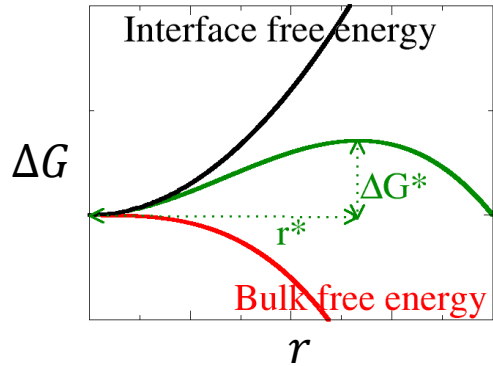
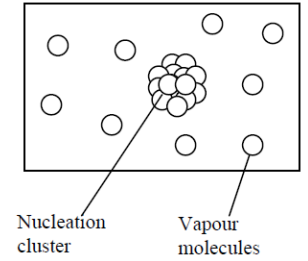


- $\Delta G^*$  represents the **energy barrier** to the nucleation process to be **overcome for the nucleation** to start
- If a spherical cluster with radius  $r < r^*$  forms by thermodynamical fluctuations, it is **unstable** and will **shrink** by losing atoms ( $r$  decreases for reducing  $\Delta G \leftrightarrow$  spontaneous process)
- Clusters with radius  $r > r^*$  have overtaken the nucleation energy barrier  $\Delta G^*$  and are **stable**. They tend to **further grow** ( $r$  increases for reducing  $\Delta G \leftrightarrow$  spontaneous process)



# Homogeneous nucleation (4)

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



Summarizing:

$$\left\{ \begin{array}{l} \Delta G_V = -\frac{k_B T}{\Omega} \ln \frac{P_V}{P_S} \Rightarrow \Delta G_V < 0 \text{ because } P_V > P_S \text{ (supersaturated vapor)} \\ r^* = -\frac{2\gamma}{\Delta G_V} \\ \Delta G^* = \Delta G(r^*) = \frac{16\pi\gamma^3}{3\Delta G_V^2} \end{array} \right.$$

$$P_V/P_S \text{ larger} \Rightarrow |\Delta G_V| \text{ larger} \Rightarrow \left\{ \begin{array}{l} r^* \text{ smaller} \Rightarrow \text{smaller size nuclei to start with, that will remain stable after growing} \\ \Delta G^* \text{ smaller} \Rightarrow \text{smaller energy barrier to surmount for the nucleation process to start with } r > r^* \end{array} \right.$$



The formation rate of stable nuclei **increases** with the  $P_V/P_S$  ratio

# Heterogeneous nucleation (1)

## Heterogeneous nucleation of a condensed film on a substrate

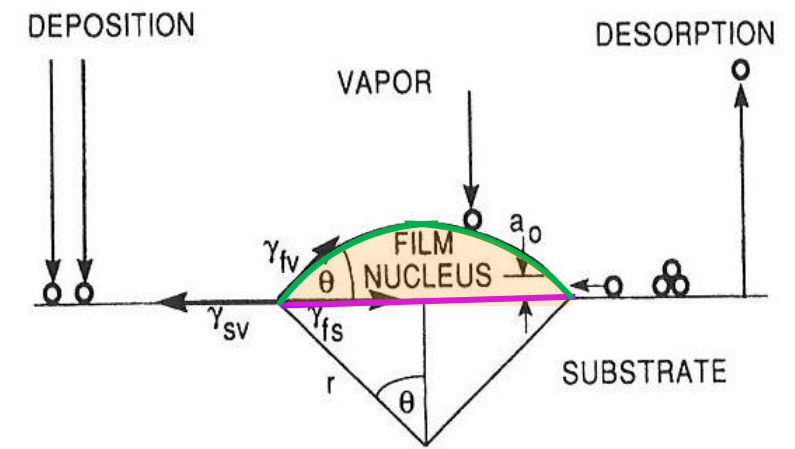
- We extend the **capillarity theory** of **homogeneous** nucleation (condensation from a vapor phase of a single chemical species – used in some CVD processes only) to a **condensed film on a substrate** → we have:
  - **two** species (substrate and depositing material)
  - **two** phases (the depositing 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 ( $<0$ ) that drives the condensation reaction (*as in homogenous nucleation*)
- $\gamma$  are the **interfacial energies per unit area** 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)

# Heterogeneous nucleation (2)

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

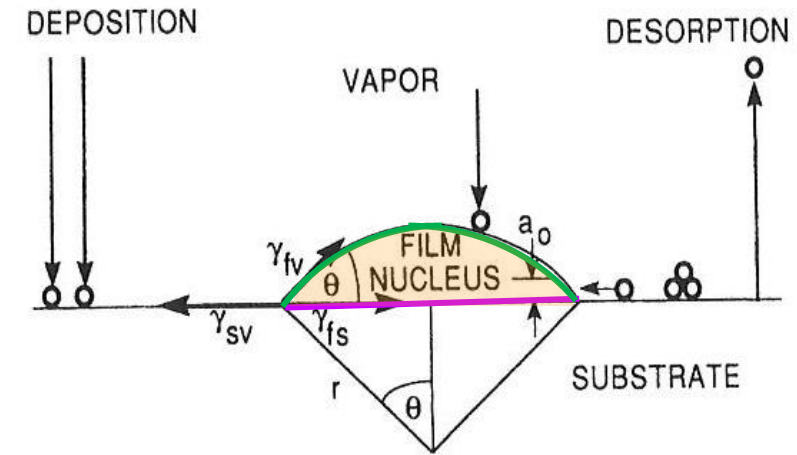
- $\Delta G_V$  is the **chemical free energy** change per unit volume
- $\gamma$  are the **interfacial tensions** between film (f), substrate (S) and vapor (V)
- $a_1 r^2$  is the curved surface area (interface f-V)
- $a_2 r^2$  is the projected area on the substrate (interface f-S)
- $a_3 r^3$  is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

For the spherical cap-shaped solid nucleus in figure:

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

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

(in terms of the surface tensions  $\sigma = \gamma$ )

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



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

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

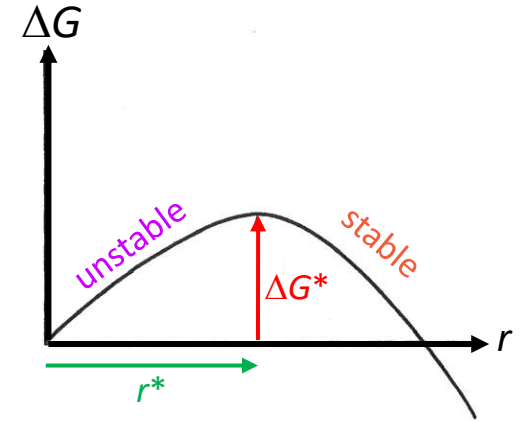
# Heterogeneous nucleation (3)

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

Looking at the stationary point of  $\Delta G$  leads to the **critical radius size** and **free energy barrier**:

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

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

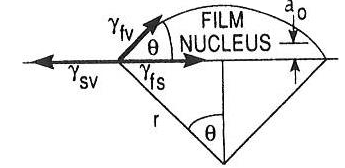


Heterogeneous nucleation behaves as homogeneous nucleation:

- $r^*$  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  $\Delta G$ )

# Heterogeneous nucleation (4)

Using the mechanical equilibrium condition parallel to substrate ( $-\gamma_{SV} + \gamma_{fS} + \gamma_{fV} \cos \theta = 0$ ) and considering the spherical cap-shaped nucleus with **wetting angle**  $\theta$ , we calculate the **critical free energy barrier**  $\Delta G^*$  as a function of the **wetting angle**  $\theta$ :

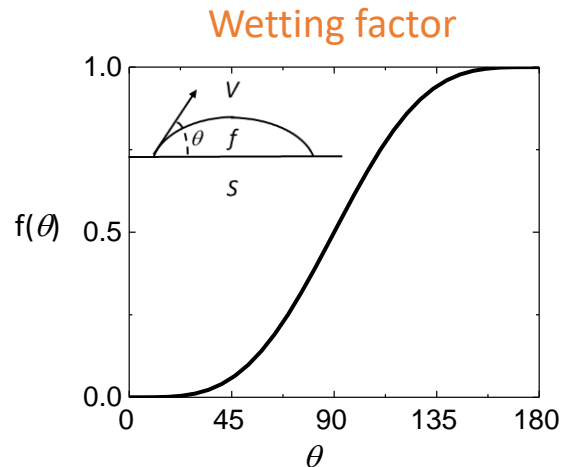


$$\Delta G^* = \frac{4 \left( 2\pi(1 - \cos \theta) \gamma_{fV} + \pi \sin^2 \theta (\gamma_{fS} - \gamma_{SV}) \right)^3}{3\pi^2(2 - 3 \cos \theta + \cos^3 \theta)^2 \Delta G_V^2} = \frac{4 \left( 2\pi(1 - \cos \theta) \gamma_{fV} - \pi \sin^2 \theta \gamma_{fV} \cos \theta \right)^3}{3\pi^2(2 - 3 \cos \theta + \cos^3 \theta)^2 \Delta G_V^2} = \frac{16\pi\gamma_{fV}^3}{3\Delta G_V^2} \frac{2 - 3 \cos \theta + \cos^3 \theta}{4}$$

[For the spherical cap-shaped solid nucleus:  $a_1=2\pi(1-\cos\theta)$ ,  $a_2=\pi\sin^2\theta$ ,  $a_3=\pi/3 (2-3\cos\theta+\cos^3\theta)$ ]

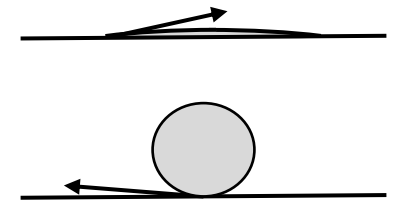
$\Delta G^*$  for homogeneous nucleation

Function of the contact (wetting) 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 (of a spherical nucleus)

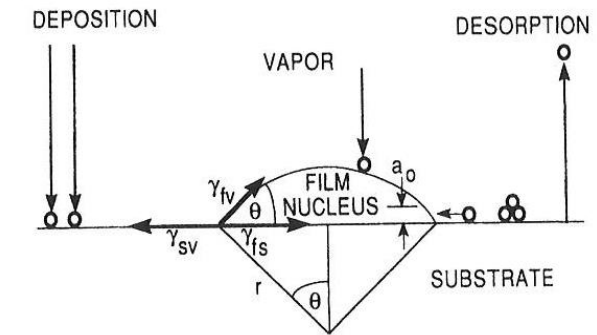


# Film growth modes (1)

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

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

Note: the wetting angle  $\theta$  depends **on the material properties only**  
(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

Note: remember that the **surface tension** in liquids, i.e. the **work required to build an area of a particular surface**, is equivalent to the **surface energy**, i.e. the **excess energy at the surface of a material compared to the bulk**.

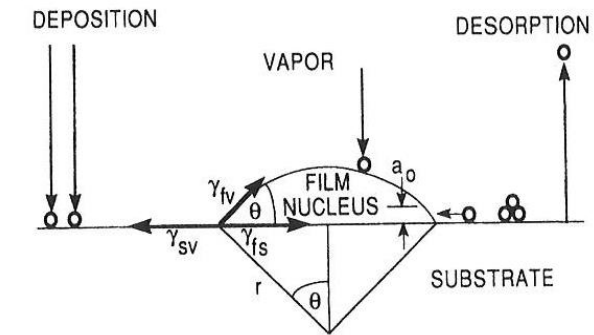
- **Layer growth:**  $\theta \approx 0 \Rightarrow \cos \theta = \frac{\gamma_{SV} - \gamma_{fS}}{\gamma_{fV}} = 1 \Rightarrow \gamma_{SV} - \gamma_{fS} = (\geq) \gamma_{fV} \Rightarrow \boxed{\gamma_{SV} \geq \gamma_{fS} + \gamma_{fV}}$

Note: if we neglect  $\gamma_{fS}$ , layer growth occurs when **the surface tension of the substrate  $\gamma_{SV}$  exceeds that of the film  $\gamma_{fV} \Rightarrow$  covering the substrate with the film leads to energy minimization because the film-vapor interface is more energetically favourable than the substrate-vapor one.**

# 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):  $\gamma_{fS} = 0, \gamma_{fV} = \gamma_{SV} \Rightarrow$  it is a special case of the **layer growth** condition in which the interface between film and substrate essentially vanishes

Note#2: 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 **layer-by-layer** (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), layered growth is *not guaranteed*

# Strain contribution to volume

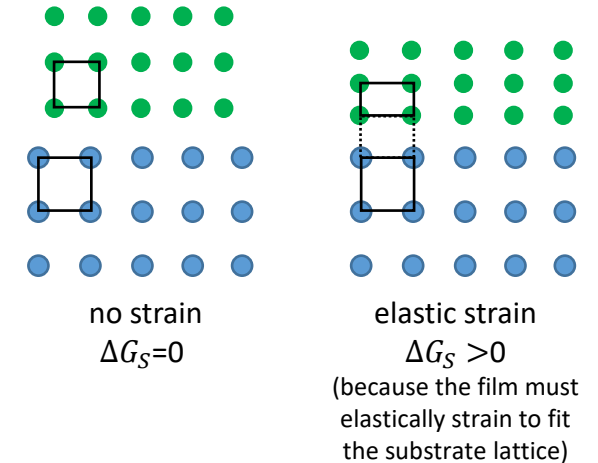
Other energy contributions (e.g. elastic strain) can be «easily» included in the free energy change expression:

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

$\Delta G_{SV}$  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** →

$$\Rightarrow \Delta G^* = \frac{4(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV})^3}{27 a_3^2 (\Delta G_V + \boxed{\Delta G_{SV}})^2} \quad \left( \text{instead of } \Delta G^* = \frac{4(a_1 \gamma_{fV} + a_2 \gamma_{fS} - a_2 \gamma_{SV})^3}{27 a_3^2 \Delta G_V^2} \right)$$



*Note:*

- $\Delta G_V < 0 \Rightarrow$  if  $\Delta G_{SV} > 0$  (e.g. because an additional energy is needed to **strain the film** to fit an unmatched substrate lattice) the energy barrier for nucleation  $\Delta G^*$  **will increase** and nucleation will be more difficult
- However, if  $\Delta G_{SV} < 0$  (e.g. because of **stress relief** during nucleation of an *initially strained substrate*, e.g. with emergent steps or dislocations) 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 within the same framework