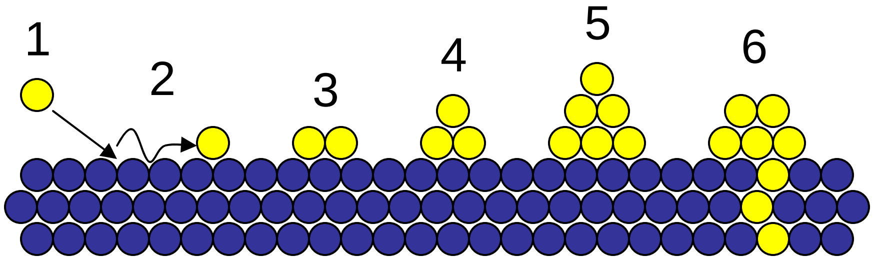
# Thin Film Growth and Evolution

# Thin Film Techniques

| **Process** | **Material** | **Uniformity** | **Impurity** | **Grain Size** | **Film Density** | **Deposition Rate** | **Substrate Temperature** | **Directional** | **Cost** |
|---|---|---|---|---|---|---|---|---|---|
| Thermal Evaporation | Metal or low melting-point materials | Poor | High | 10 ~ 100 nm | Poor | 1 ~ 20 A/s | 50 ~ 100 °C | Yes | Very low |
| E-beam Evaporation | Both metal and dielectrics | Poor | Low | 10 ~ 100 nm | Poor | 10 ~ 100 A/s | 50 ~ 100 °C | Yes | High |
| Sputtering | Both metal and dielectrics | Very good | Low | ~ 10 nm | Good | Metal:<br>~ 100 A/s<br>Dielectric:<br>~ 1-10 A/s | ~ 200 °C | Some degree | High |
| PECVD | Mainly Dielectrics | Good | Very low | 10 ~ 100 nm | Good | 10 - 100 A/s | 200 ~ 300 °C | Some degree | Very High |
| LPCVD | Mainly Dielectrics | Very Good | Very low | 1 ~ 10 nm | Excellent | 10 - 100 A/s | 600 ~ 1200 °C | Isotropic | Very High |

# Steps of Thin Film Growth

1. Absorption (physisorption)
2. Surface diffusion
3. Chemical bond formation (chemisorption)
   - Molecule-molecule
   - Substrate-molecule
4. Nucleation
5. Microstructure formation
   - Crystal structure
   - Defects
6. Bulk changes
   - Diffusion
   - Grain growth



# Physisorption

- An approaching atom can either be
  - reflected or
  - absorbed

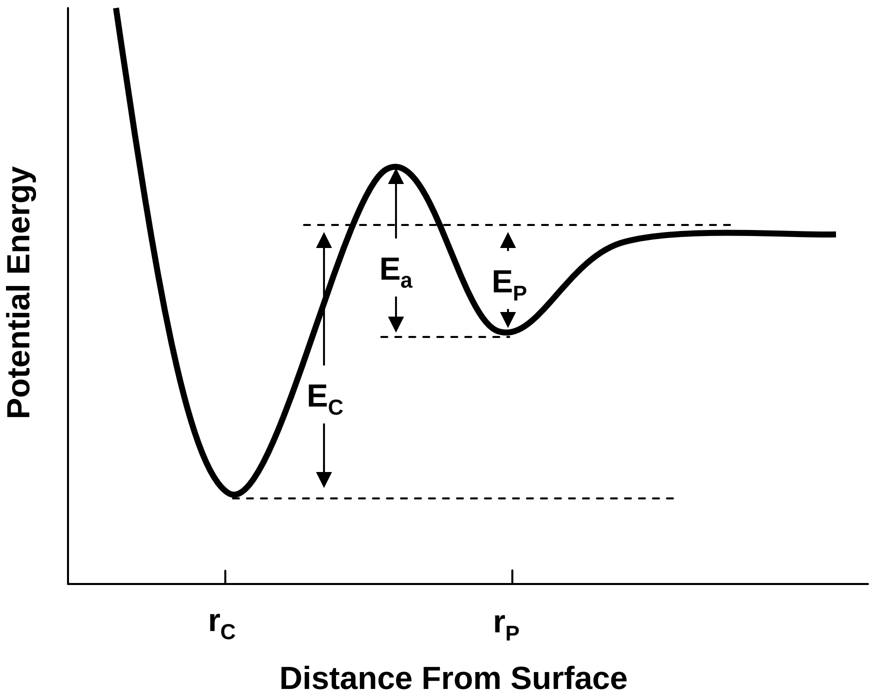
  on to the surface of the substrate.
- The process is dependent on
  - the incoming flux of atoms
  - the trapping probability
  - the sticking coefficient

# Energy Barriers

- Once physisorbed, the atom can be chemisorbed or desorbed (ejected).
- Both physisorption and chemisorption have to overcome local energy barriers.

$$k_r = v \exp\left(\frac{-E_b}{kT}\right)$$

$$\tau_r = \frac{1}{k_r} = \frac{1}{v}\exp\left(\frac{E_b}{kT}\right)$$



- $E_P$ ~ 0.25 eV
- $E_C$ ~ 1 - 10 eV

# Adsorption Effects

- Whether physical or chemical, adsorption is counterbalanced by desorption.
- If *P* is the partial pressure of the atoms in the vapor phase and $k_{\text{ads}}$ and $k_{\text{des}}$ the adsorption and desorption rates, then the surface coverage percentage, $\theta$, as a function of time is,

$$\theta = \frac{KP}{1+KP}\left\{1 - \exp\left[-k_{des}\left(1+KP\right)t\right]\right\} \qquad K = \frac{k_{ads}}{k_{des}}$$

- If *KP* >> 1 then coverage is unity. At very long times, the equilibrium coverage is,

$$\theta = \frac{KP}{1+KP}$$

# Surface Energy

- Once an atom sticks to the surface, it creates a tension (energy) in the surface.
- It is due to the surface atoms stretching their bonds in response to the absorption of the atom.
- It is a function of the broken bond energy of exposed surface atoms which depends on the crystal structure of the substrate.

# Surface Diffusion

- Overall surface energy can be minimized if the atom has enough energy and time to diffuse to a low energy site.
- The diffusion rate increases with temperature.
- A diffusion length can be defined as:

$$\Lambda = a\sqrt{k_s t}$$

where $k_s$ is the diffusion rate, $t$ is diffusion time and $a$ is the hop distance.

# Peak in Surface Diffusion

- At low temperatures, the diffusion length increases with temperature.
- At higher temperatures, the desorption rate also increases and overtakes absorption. Therefore, the diffusion length decreases.
- Typical diffusion lengths:
  - Physisorption : 300 μm
  - Chemisorption : 5 nm

# From Atom to Film

- Since adding an atom to the surface creates extra surface energy, there must be a driving force to overcome this barrier.
- The exact nature depends on the deposition technique:
  - PVD: The atom or molecule should have a lower chemical potential as a condensate than as a vapor.
  - CVD: The solid form should be thermodynamically predicted over the gas form.

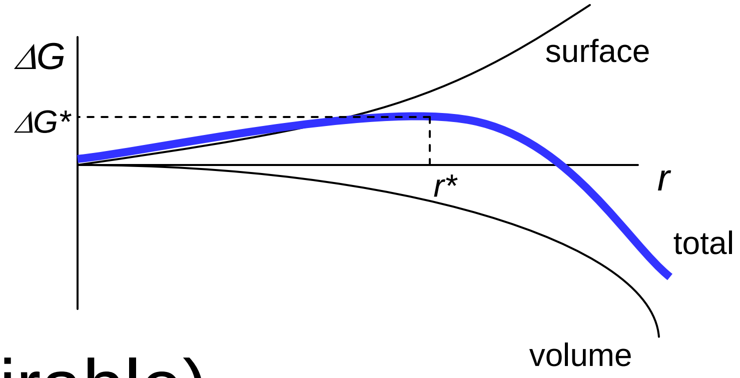
# Nucleation

- For a stable film, nuclei at a critical size are needed.
- For “embryos” smaller than this, the surface energy is too large and the overall reaction is thermodynamically unfavorable.
- A stable embryo is one which adding more molecules decreases the Gibb’s free energy.

# Nucleation Types

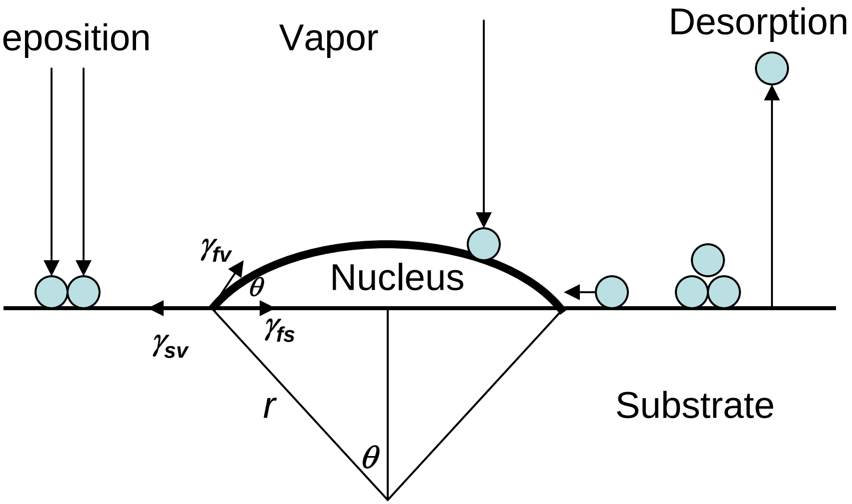
- Homogeneous (undesirable)
  - The free energy of the atoms in free standing (gas) form is smaller when they nucleate.

$$\boxed{\Delta G_{total} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma}$$



- Heterogeneous (desirable)
  - Nucleation on the substrate surface in solid form reduces the surface energy by reducing the surface area.

# Heterogeneous Nucleation



- Nucleation depends on the relative surface energies of the various interfaces:
  - Substrate-vapor
  - Film-substrate
  - Film-vapor

$$\boxed{\Delta G_{total} = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}}$$

- It has a barrier behavior similar to homogeneous nucleation with a critical radius and energy.

$$r^* = \frac{-2\left(a_1 \gamma_{fv} + a_2 \gamma_{fs} - a_2 \gamma_{sv}\right)}{3 a_3 \Delta G_v}$$

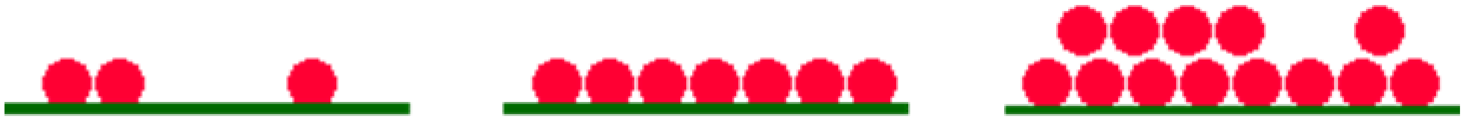
$$\Delta G^* = \frac{16\pi\left(\gamma_{fv}\right)^3}{3\left(\Delta G_v\right)^2}\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\}$$

# Dependence of Nucleation on Growth Parameters

- Substrate Temperature
  - The critical nuclei size increases with temperature.
  - The barrier for nucleation is greater with increasing temperature.
- Deposition Rate
  - The critical nuclei size decreases with increasing deposition rate.
  - The barrier for nucleation is smaller with increasing deposition rate.

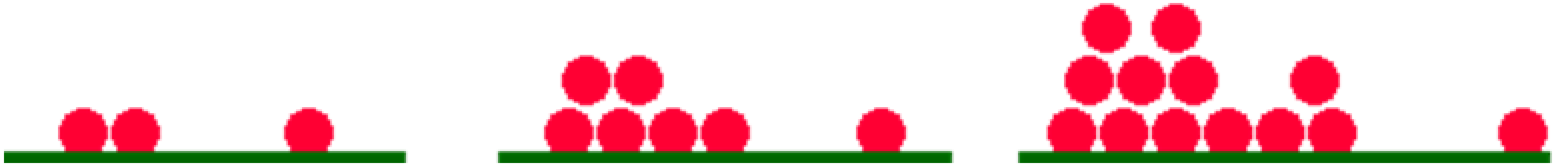
# Frank van der Merwe (Layers)

- If the substrate-vapor surface energy is larger than the other two combined.
- A smooth film will form.
- Layered growth will occur.
- The film wets the surface to lower surface energy.



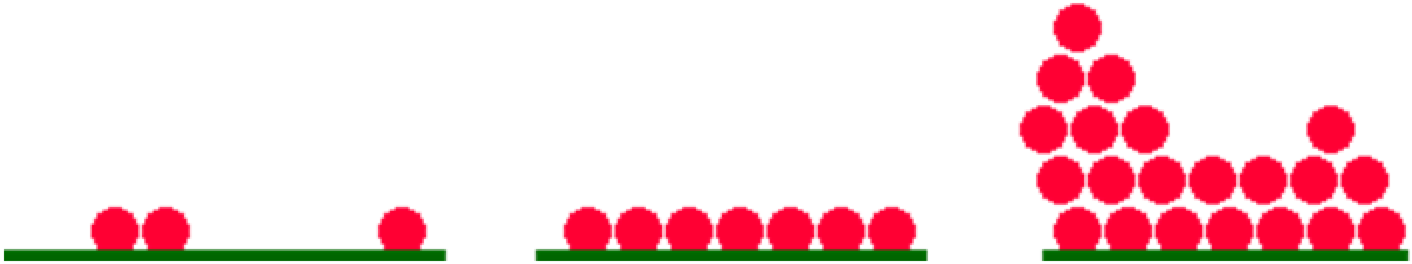
# Volmer Weber (Islands)

- The total surface energy of the film interfaces is larger than that of the substrate-vapor interface.
- The material balls up to minimize interface with the substrate.
- Uneven growth.
- Slow diffusion.



# Stranski-Krastanov (mixed)

- Initial layer growth.
- Changes into island growth after a few monolayers.
- The initial layer is strained to match the substrate. After a few layers, the strain is relaxed.



# Kinetics of Nucleation

- The nucleation rate is a product of three terms.

$$\boxed{\dot{N} = N^{*} A^{*} \omega}$$

where *N** is the equilibrium concentration of the stable nuclei, $\omega$ is the rate at which atoms impinge on to the nuclei of critical area *A**.

$$N^{*} = n_s \exp\left(-\Delta G^{*} / k_B T\right)$$

$$A^{*} = 4\pi\left(r^{*}\right)^2$$

$$\omega = \frac{\alpha\left(P_V - P_S\right) N_A}{\sqrt{2\pi MRT}}$$

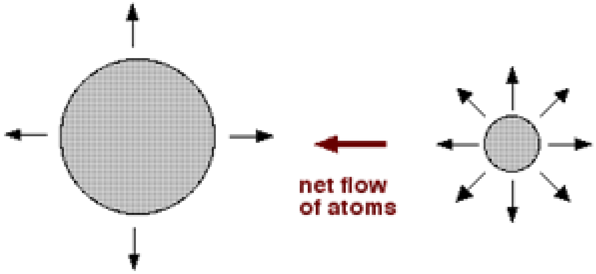
where $\alpha$ is the sticking coefficient, $N_A$ is the Avogadro’s number and *M* is the atomic weight

# Microstructure

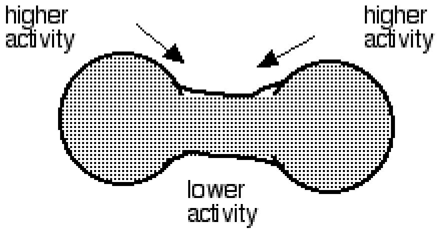
- Higher substrate temperatures favor fewer, larger nuclei.
- Higher deposition rates favor more, smaller nuclei.
- To get single crystal or large grained polycrystalline films, you need higher temperatures and slower deposition rates.
- On the other extreme, you’ll get fine grained polycrystalline films.

# Nuclei Combination

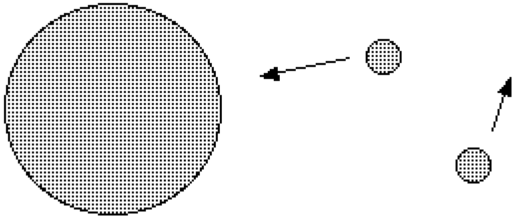
- Ostwald Ripening
  - Small particles shrink, large ones grow.



- Sintering
  - A neck forms between two growing nuclei.
  - The neck's curvature allows for faster growth and merging.



- Cluster Coalescence
  - Nuclei also undergo surface diffusion
  - When it is chemically favorable for two nuclei to align and stay permanently at a location, they merge.



# Film Morphology

- The nucleation and the subsequent combination of the nuclei lead to a final film microstructure.
- This morphology is influenced by:
  - Substrate temperature
  - Deposition rate
  - Geometry
  - Desorption
  - Bulk and surface diffusion
- Generally, four different classes of film morphology exist.

# Film Morphology: Z1

- Conditions:
  - $T_s/T_m$ low, little surface diffusion
  - Evaporation: $T_s/T_m < 0.3$
  - Sputtering
    - $T_s/T_m < 0.1$ at lower pressure
    - $T_s/T_m < 0.4$ at higher pressure
- Small diameter (~ 10nm) columns with poor crystallinity or amorphous structure
- Columns have voided boundaries.
- Dome tops above columns
- Created by surface roughness, line of site deposition
- High dislocation density leading to a hard material.

# Film Morphology: ZT

- Conditions:
  - Sputtering only
    - $0.1 < T_s/T_m < 0.4$ at lower pressure
    - $0.4 < T_s/T_m < 0.5$ at higher pressure
- Voids and domes are reduced
- The columns have fibrous grains and dense grain boundaries.
- Still high dislocation density leading to a hard material.

# Film Morphology: Z2

- Conditions:
  - Surface diffusion is becoming important.
  - Evaporation
    - $0.3 < T_s/T_m < 0.5$
  - Sputtering
    - $0.4 < T_s/T_m < 0.7$
- Columns with tight grain boundaries. Voids are filled by surface diffusion.
- Fewer defects.
- Faceted column tops.

# Film Morphology: Z3

- Conditions:
  - Surface diffusion is high to allow for annealing.
  - Evaporation
    - $T_s/T_m > 0.5$
  - Sputtering
    - $0.6 < T_s/T_m < 1$
- Preferred grains grow at the expense of others, leading to large grains.
- Smoother surfaces.
- Fewer dislocations leading to softer films.

# Morphology Summary