

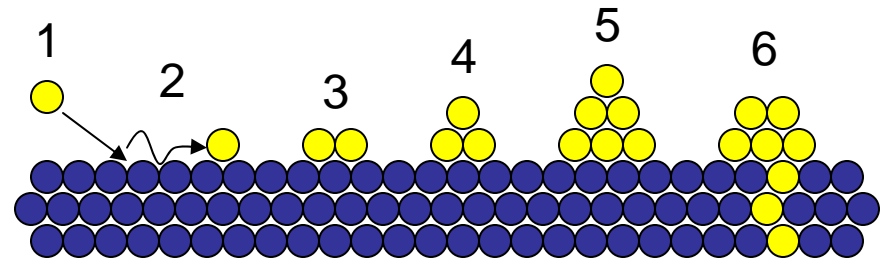
Thin Film Growth and Evolution

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: ~ 100 A/s Dielectric: ~ 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

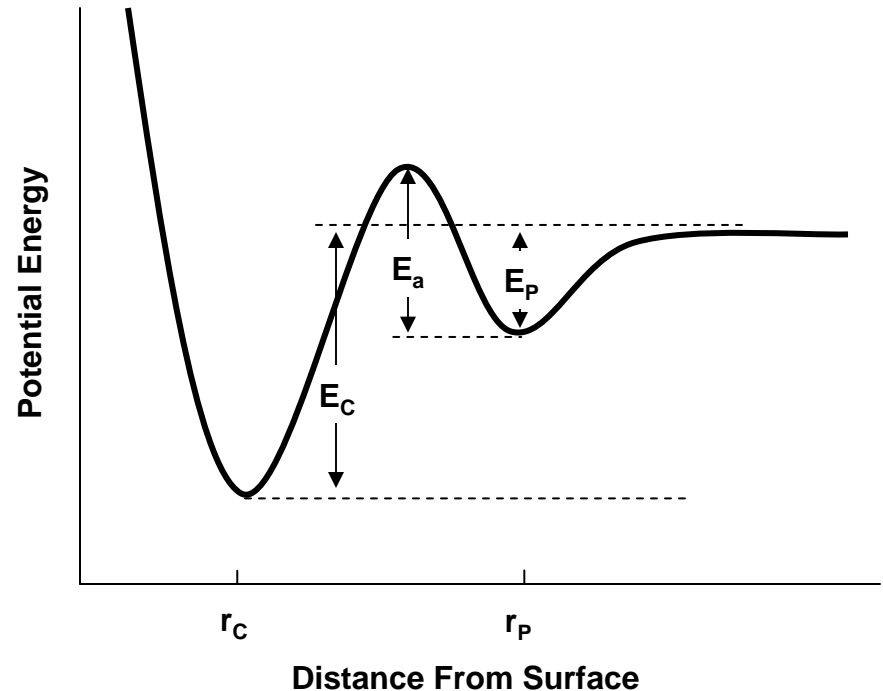
- An approaching atom can either be
 - reflected or
 - absorbedon to the surface of the substrate.
- The process is dependent on
 - the incoming flux of atoms
 - the trapping probability
 - the sticking coefficient

Energy Barriers

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

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

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



- $E_p \sim 0.25$ eV
- $E_c \sim 1 - 10$ 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_{ads} and k_{des} the adsorption and desorption rates, then the surface coverage percentage, θ , as a function of time is,

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

- If $KP \gg 1$ 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.

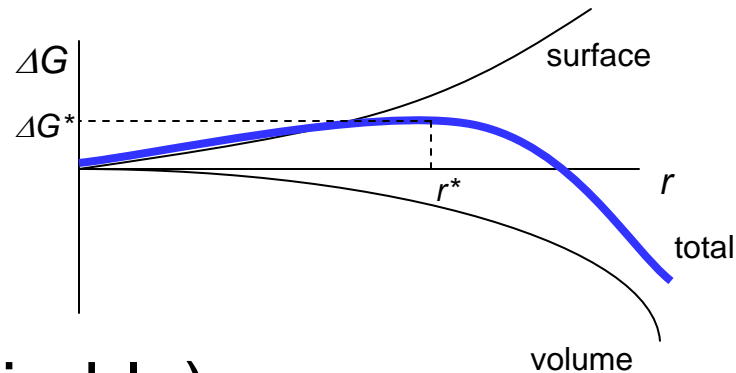
Nucleation

- 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.

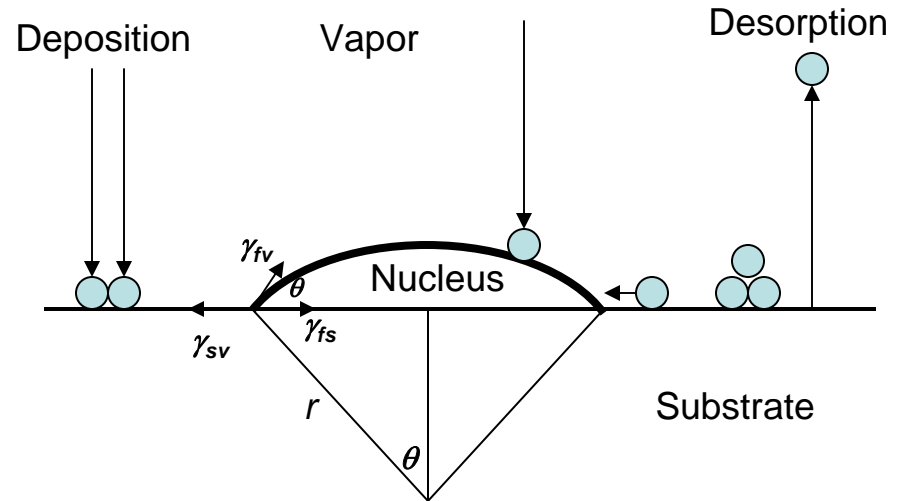
$$\Delta G_{total} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$



- 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



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

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

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

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

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.

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

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

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

$$A^* = 4\pi(r^*)^2$$

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

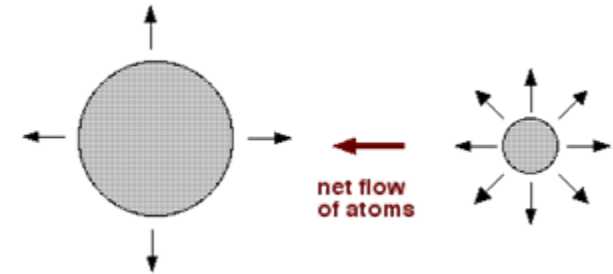
where α is the sticking coefficient, N_A is the Avogadro's number and M is the atomic weight

Microstructure

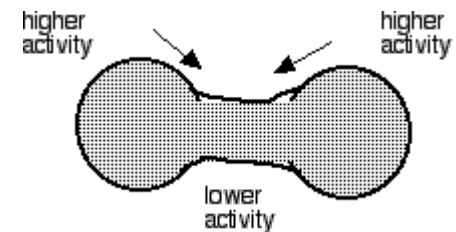
- Higher substrate temperatures favor fewer, larger nuclei.
- Higher deposition rates favor more, smaller nuclei.
- To get single crystal or large grained polycrystalline films, you need higher temperatures and slower deposition rates.
- On the other extreme, you'll get fine grained polycrystalline films.

Nuclei Combination

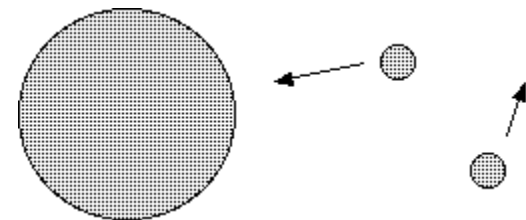
- Ostwald Ripening
 - Small particles shrink, large ones grow.



- 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 ($\sim 10\text{nm}$) 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

