Nucleation – Concept of Surface Energy

Differential Energy dE cost for creating a surface are dA

$$dE = TdS - PdV + \gamma dA$$

$$dG = -SdT + VdP + \gamma dA$$

$$dG = \gamma dA$$

$$dE = \delta W = \gamma dA$$

$$Fdx = \gamma dA = \gamma(2b)dx$$

$$\gamma = \frac{F}{2b}$$

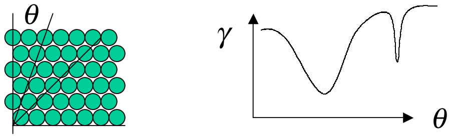
Force per unit length of the circumference (N/m) is the surface tension and in case of the liquids surface energy per unit area (J/m^2) is the same as the surface tension

Physical understanding of the origin of surface energy

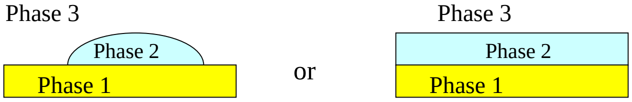
- Why is there a surface energy associated with solid surfaces?
- What is the physical explanation/interpretation?
- No bonds from the top. Compared to bulk the bonding may not be satisfied.
- Surface energy tries to minimize itself by diffusion. If surface diffusion is fast the nuclei will expose the lowest energy surfaces.
- γ depends on
  - ⇒ Chemical composition
  - ⇒ Atomic scale roughness
  - ⇒ Atomic scale reconstruction
  - ⇒ Crystallographic orientation
- Example: (111) plane of an FCC structure is the closest pack plane. The # of bonds in the plane is maximized and the number out of the plane are minimized. Consequently $\gamma_{fcc}^{111} < \gamma_{fcc}^{100}$

Physical understanding of the origin of surface energy

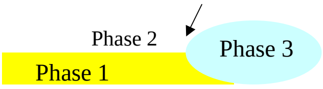
- Charge neutrality @ the surface leads to lower γ.
- In crystals having ionic bonds (NaCl, CaF_2) or polar bonds (GaAs, ZnO) g tends to be lower for faces that contain equal numbers of cations (Na, Ca, Ga, Zn) and anions (Cl, F, As, O).
- i.e., nonpolar surfaces are lower energy.
- γ for a particular surface may be lower than predicted from the dangling bond density because crystal surfaces rearrange (called reconstruction) such that termination does not necessarily have the geometry of the atomic arrangements of the cleaved plane in the bulk crystal.
- γ is lower for low index planes called singular surfaces



Nucleation



At constant P and T dG < 0 for nucleation to occur



create area dA of 1-2 and 2-3 interface

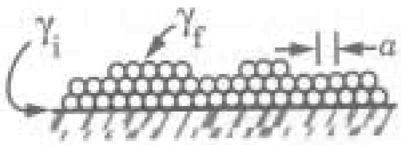
$$G_{before} - G_{after} = [\gamma_{13} - (\gamma_{12} + \gamma_{23})]dA$$

$[\gamma_{13} - (\gamma_{12} + \gamma_{23})] \geq 0$ ⇨ Phase 2 spreads over phase 1 completely “wetting” it

$[\gamma_{13} - (\gamma_{12} + \gamma_{23})] < 0$ ⇨ Phase 2 remains in a lens configuration

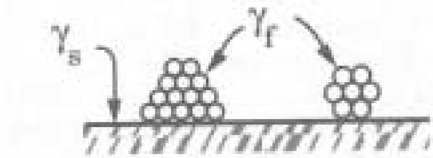
Film Growth Modes

$$\gamma_{13}=\gamma_s \quad \gamma_{12}=\gamma_i \quad \gamma_{23}=\gamma_f$$



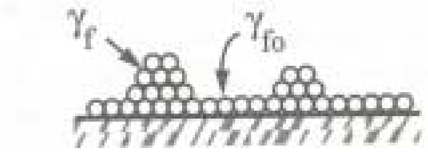
$$\boxed{\gamma_s \geq (\gamma_i+\gamma_f)}$$

Frank van der Merwe
(layer by layer growth)



$$\boxed{\gamma_s < (\gamma_i+\gamma_f)}$$

Volmer-Weber
(island growth)



1st

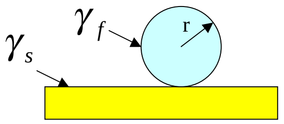
$$\boxed{\gamma_s \geq (\gamma_i+\gamma_{fo})}$$

$$\boxed{\gamma_s < (\gamma_i+\gamma_f)}$$

later

Stranski-
Krastanov
growth

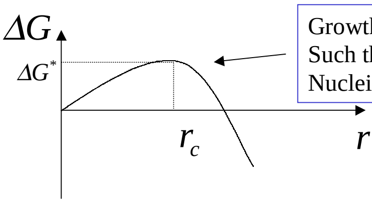
Nucleation: the critical radius



Assume that $\boxed{\gamma_s < (\gamma_i+\gamma_f)}$

$$\Delta G=(\mu^s-\mu^v)\frac{1}{\tilde{V}_s}\frac{4}{3}\pi r^3+\gamma_f 4\pi r^2$$

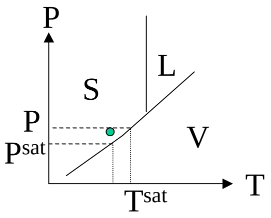
$$\Delta G=-\Delta\mu\frac{1}{\tilde{V}_s}\frac{4}{3}\pi r^3+\gamma_f 4\pi r^2 \quad where \quad \Delta\mu=\mu^v-\mu^s$$



Growth after r_c decreases the ΔG
Such that nuclei that have $r>r_c$ grow
Nuclei with $r<r_c$ are subcritical and disappear

$$r_c=\frac{2\gamma_f}{(\Delta\mu/\tilde{V}_s)}$$

Nucleation rate



$$\Delta G^* = \frac{16}{3}\frac{\pi\gamma_f^3}{(\Delta\mu/\tilde{V}_s)^2}$$

$$\Delta\mu = \mu^v - \mu^s$$

$$\mu^v = \mu^o(P^o,T) + RT\,ln(P/P^o)$$

$$at \quad P = P^{sat} \quad \mu^s = \mu^v = \mu^o(P^o,T) + RT\,ln(P^{sat}/P^o)$$

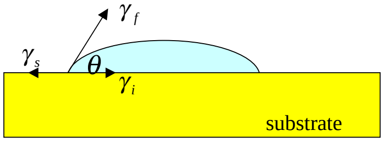
$$\rightarrow \Delta\mu = RT\,ln(P/P^{sat}) \rightarrow \Delta G^* = \frac{16}{3}\frac{\pi\gamma_f^3}{\left\{\frac{RT\,ln(P/P^{sat})}{\tilde{V}_s}\right\}^2}$$

Another way of looking at it

$$\Delta\mu \propto \Delta T \qquad r_c \propto \frac{2\gamma_f}{\Delta T} \qquad \Delta G^* \propto \frac{\gamma_f^3}{(\Delta T)^2}$$

Nucleation rate $\rightarrow$ $R_n \propto e^{-\Delta G^*/RT}$

Nucleation morphology



Assuming amorphous or liquid nuclei one can do a force balance in the direction parallel to the surface

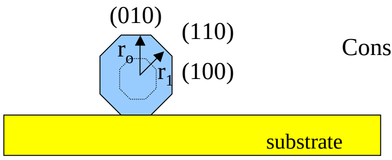
$$\gamma_s = \gamma_i + \gamma_f\cos\theta$$

While we can equate surface energy with surface tension in liquids this is not the case with solids. For solids there is also a quantity called surface stress.

In solids surface energy is anisotropic and the shape of the nuclei will adjust to minimize the energy of the total surface area through

$$\sum_k \gamma_k A_k = minimum$$

Nucleation morphology



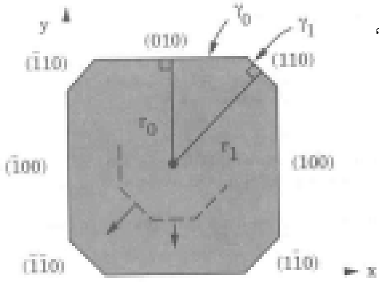
Consider the case of poor wetting A_i=0

$$\boxed{\sum_k \gamma_k A_k = minimum}$$

$$\Downarrow$$

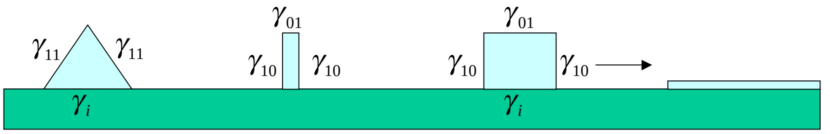
$$\boxed{\frac{\gamma_k}{r_k} = constant}$$

'Wulff Theorem"



- $\gamma_1 = 1.2\ \gamma_o$
- Higher energy surfaces tend to grow faster. They tend to be higher index surfaces.
- Faster growing faces grow themselves out of existence

Island Nucleation & 2-D nucleation

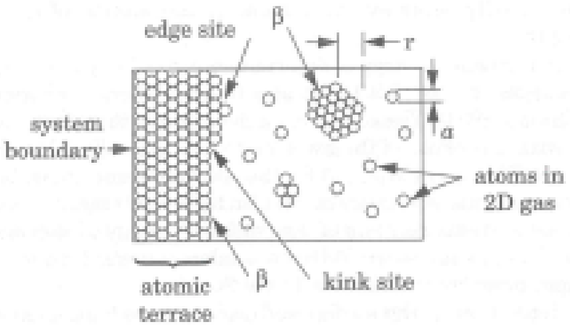


$\gamma_{01} << \gamma_{11} \approx \gamma_i$

$\gamma_{10} << \gamma_{01} \approx \gamma_i$

$\gamma_{10} << \gamma_{01} < \gamma_i$

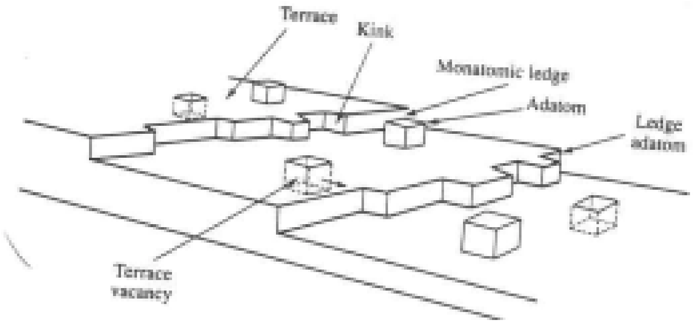
$\gamma_{01} \approx \gamma_{10} \approx \gamma_i$



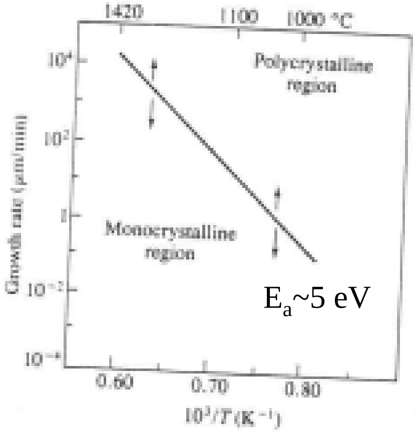
2-D Nucleation

Frank van der Merwe
(layer by layer growth)

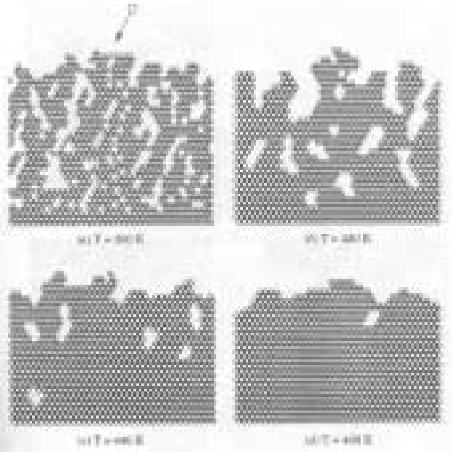
Epitaxy



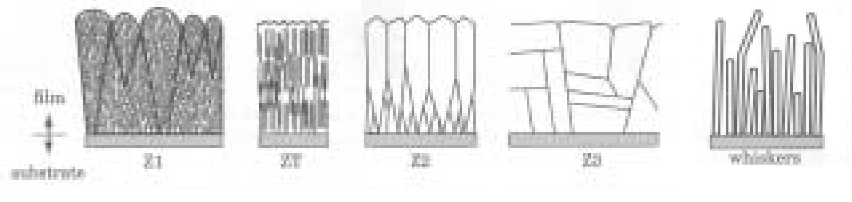
Film crystallinity



E_a~5 eV



Film Morphology - Growth Zones



- Z1: T_s/T_m so low that surface diffusion is negligible (Λ<a). ~10 nm columns (poor crystallinity or amorphous) separated by ~1-2 nm voids. Columns terminate in domes at the top
- ZT: like Z1 but domes and voids are absent. Common in energy-enhanced deposition methods (plasma, sputtering, etc.)
- Z2: occurs for T_s/T_m>0.3, surface diffusion is significant, Tight columns with grain boundaries, column diameter ↑with T_s ↑. Columns less defected than Z1 or ZT and faceted at top. The boundaries are planes of reduced bonding rather than planes of xtallographic discontinuity.
- Z3: occurs for T_s/T_m>0.5, significant bulk annealing takes place, isotropic and equiaxed xtals. Films are smoother.