Chapter 5
DEPOSITION

Six sequential substeps:

1) Adsorption
2) Surface diffusion
3) Reaction Nucleation
4) Morphology development
5) Film-substrate inter-diffusion
6) Remember the balance in thermodynamics and kinetics: to achieve a thermodynamically stable configuration, we do not want kinetic limits to play important roles; to avoid a stable configuration, we want to use the kinetic limits.

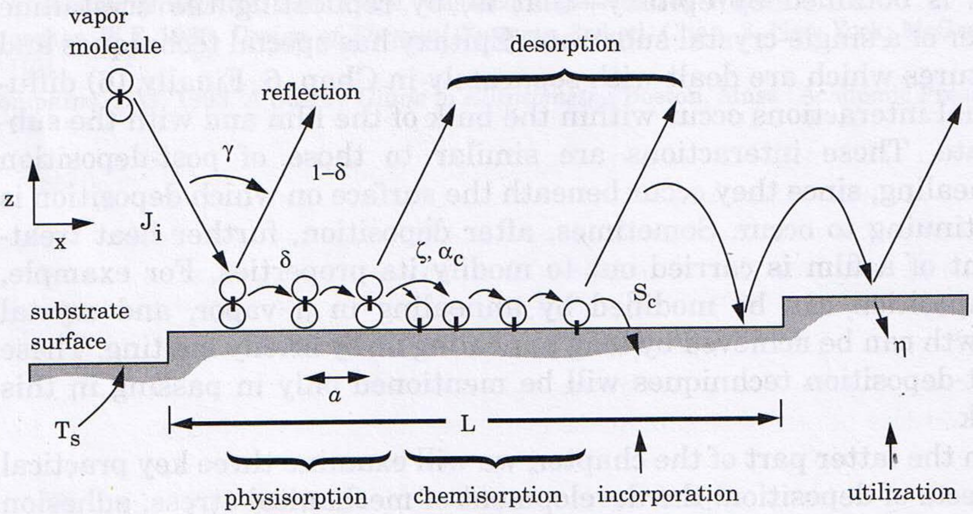
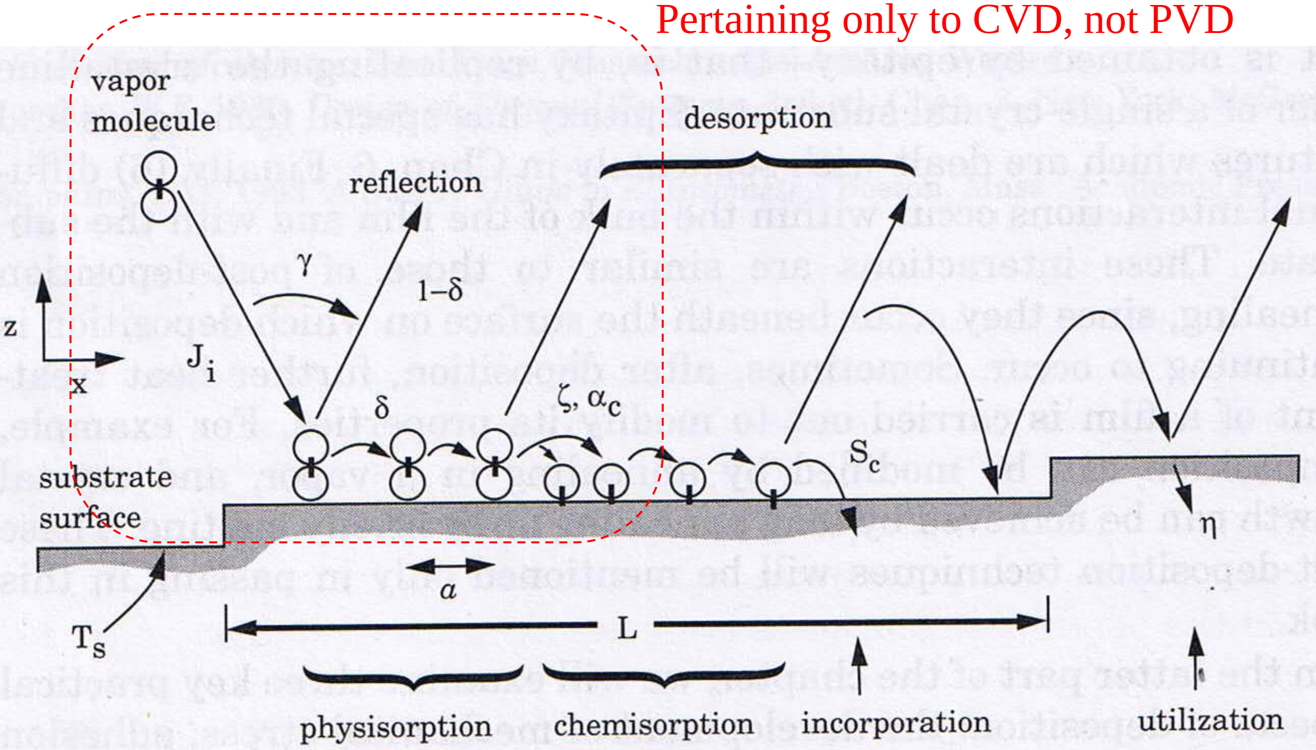


Figure 5.1 Adsorption processes and quantities. α_c is used only for condensation (adsorption of a material onto itself). A vertical connecting bar denotes a chemical bond.

5.1. Adsorption

See the illustration of the various processes at the substrate surfaces (Fig. 5.1).

Characteristics: the lacking of or weak chemical bonding between the incoming molecules with the substrate surface with the incoming molecules remaining in the molecular states.



Pertaining only to CVD, not PVD

Figure 5.1 Adsorption processes and quantities. α_c is used only for condensation (adsorption of a material onto itself). A vertical connecting bar denotes a chemical bond.

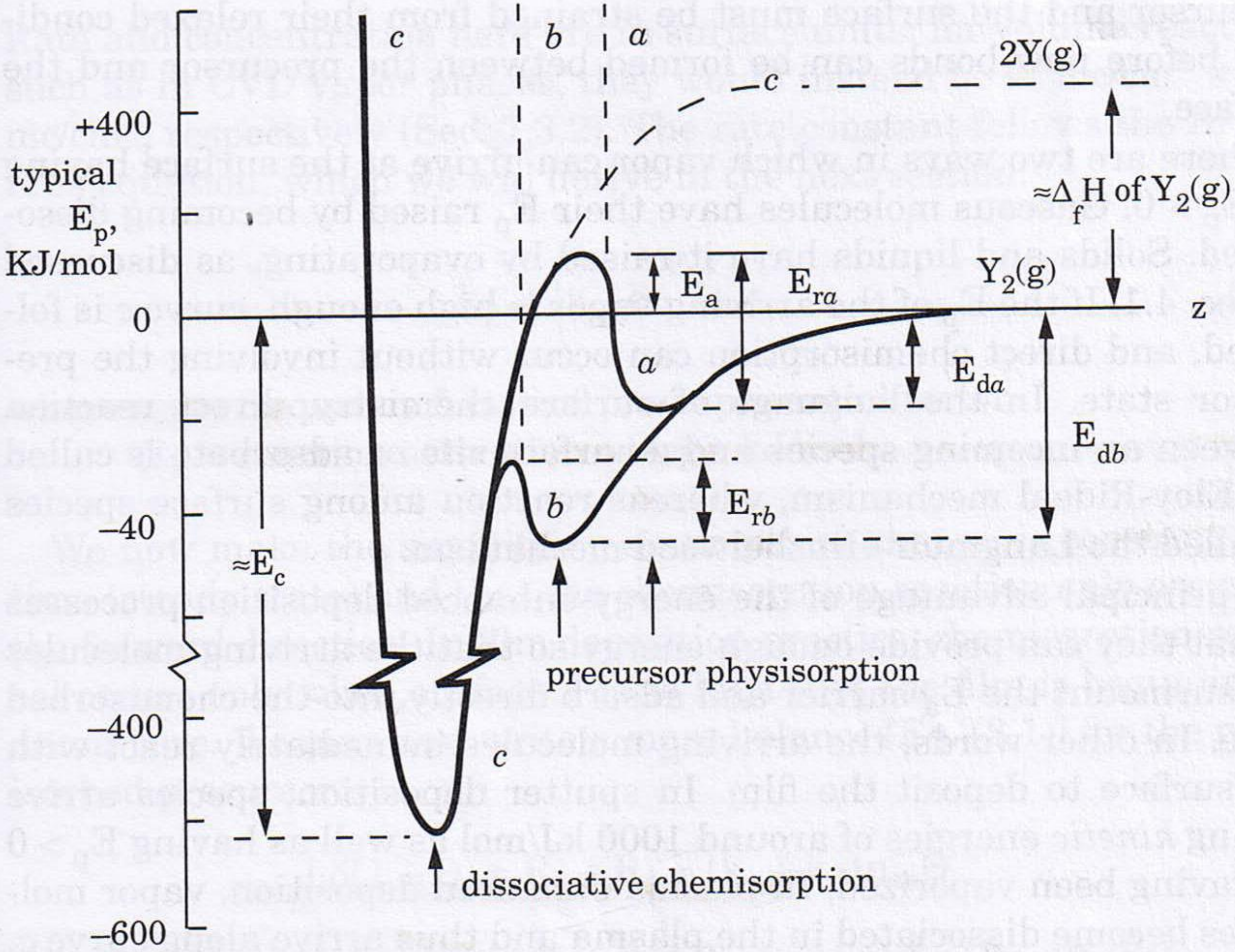


Figure 5.2 Energetics of the precursor adsorption model. Energy scale is typical only.

5.5.1. Definition of Symbols

1. **δ-** trapping probability (the fraction of the arriving vapor that becomes physisorbed *on surface that is not covered by adsorbant* $(1 - \Theta)$
2. **α_c** - condensation coefficient (the fraction of the arriving vapor that becomes incorporated into its own condensed phase); we encountered this during the discussion of evaporation;
3. **Sc** - sticking coefficient (i.e. α_c for the duration of the experiment);
4. ζ (zeta) - chemisorption reaction probability on surface that is not covered by adsorbant $(1 - \Theta)$; (it is the α_c in the case in which the vapor and the substrate are different); e.g. H_2O on surfaces at RT;

5.5.1. Definition of Symbols (cont'd)

At vapor-solid equilibrium (**$p=p_v$**), the amounts of the material in solid phase and that in vapor phase remain constant with time. Therefore, every molecule condenses will eventually be re-evaporated, i.e. $S_c \rightarrow 0$, although $\alpha_c > 0$.

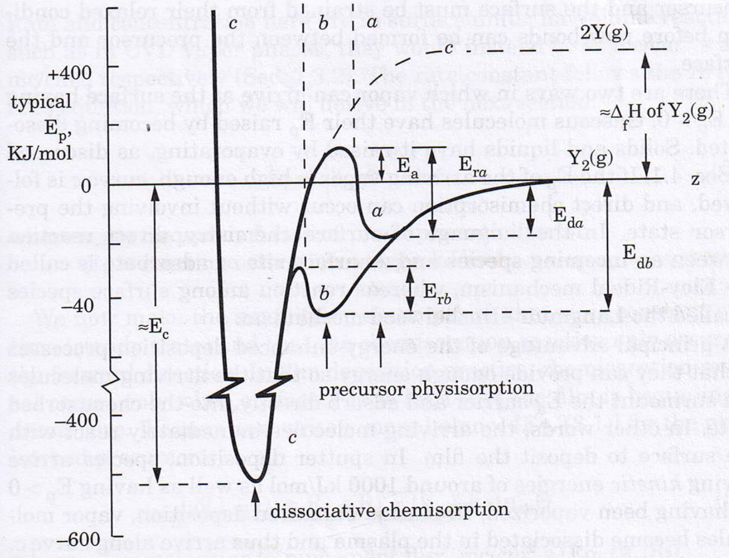
During continuous deposition(**$p>p_v$**) , i.e. the reaction proceeds in the direction of vapor goes into solid, S_c becomes fraction incorporated; S_c has a clear significance for practical film deposition, but much less of a fundamental significance comparing to, e.g. δ and ζ.

The usefulness of α_c has been demonstrated during the discussion of the temperature dependence of the Knudsen cell flux.

1. **δ-** trapping probability (the fraction of the arriving vapor that becomes physisorbed)
2. **α_c** - condensation coefficient (the fraction of the arriving vapor that becomes incorporated into its own condensed phase)
3. **Sc** - sticking coefficient (i.e. **α_c** for the duration of the experiment);
4. ζ (zeta) - chemisorption reaction probability on surface that is not covered by adsorbant (1 - Θ); (it is the α_c in the case in which the vapor and the and the substrate are different)

5.1.2. Molecule-substrate interaction (Figure 5.2)

- Fig.5.2 is for the hypothetical case of diatomic gas molecules reacting with a substrate surface.
- Zero potential energy $E_p = 0$ is taken as Y_2 infinitely far away from the substrate.
- The system is in a higher energy state when Y_2 is in the atomic state Y (by the amount equals to the formation enthalpy of Y_2), as if curve c is extended to infinitely large distance.
- Case a is called activated process because $E_a > 0$, whereas case b is not activated even though there is an energy barrier for incorporation in both cases E_{ra} and E_{rb}. The difference is whether a molecule will decompose to become part of the film or to escape from the surface (desorption).



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5.1.3. Derivation of the rate of reaction

The general expression for a first order chemical reaction is:

$$R_k = k_k n_s = k_k n_{s0}\Theta$$

where R_k is the rate of the k^{th} reaction in mc/cm^2•s. n_s is the surface concentration of reactant in mc/cm^2;

n_{so} is the monolayer coverage of reactant in mc/cm^2;

Θ is the fractional surface coverage by reactant aka **adsorption isotherm**.

The rate constant, k_k, follows that Arrhenius equation:

$$k_k = v_{ok} e^{-E_k / RT}$$

v_{ok} is the pre-exponential factor;

E_k is the reaction activation energy in kJ/mol;

(Θ is a quantity of similar nature to the vapor pressure of an evaperant in a Knudsen cell. It is like a measure of the water level in a bucket that is being filled by a tap while being drained by a hole at the bottom.)

A first-order reaction means that R is proportional to n_s, the concentration of one of the reactants.

Now assuming steady state n_s does not vary with time, we can write the mass balance equation for the surface adsorbed precursor:

$$J_i \delta (1 - \Theta) = R_r + R_d = (k_r + k_d) n_{so} \Theta$$

Subscripts r means reaction and d means desorption. Here we assumed no adsorption in the area occupied by adsorbate (Θ). Θ is analogous to the pressure in a vacuum chamber that is determined by the combination of the gas supply rate and the pump capacity. Here, Θ is determined by J_i, R_r and R_d.

$$\therefore \Theta = \frac{J_i \delta / n_{so}}{J_i \delta / n_{so} + k_r + k_d}$$

$$\therefore R_r = k_r n_{s0} \Theta = \frac{k_r J_i \delta}{J_i \delta / n_{so} + k_r + k_d}$$

5.1.4. Implication

- Activated reaction: $E_r – E_d > 0$ (case a), and R_r decreases with increasing $E_r – E_d$ and decreasing temperature, i.e., thermally activated. IncreasingT favors the process with higher activation energy.

- In the case of not activated (case b), R_r decreases with increasing temperature.

- All the above discussions are under the assumption of low surface coverage Θ.

$$R_r \approx \frac{J_i \delta}{1+\frac{\nu_{od}}{\nu_{or}} e^{+(E_r - E_d)/RT}} \propto e^{-(E_r - E_d)/RT}$$

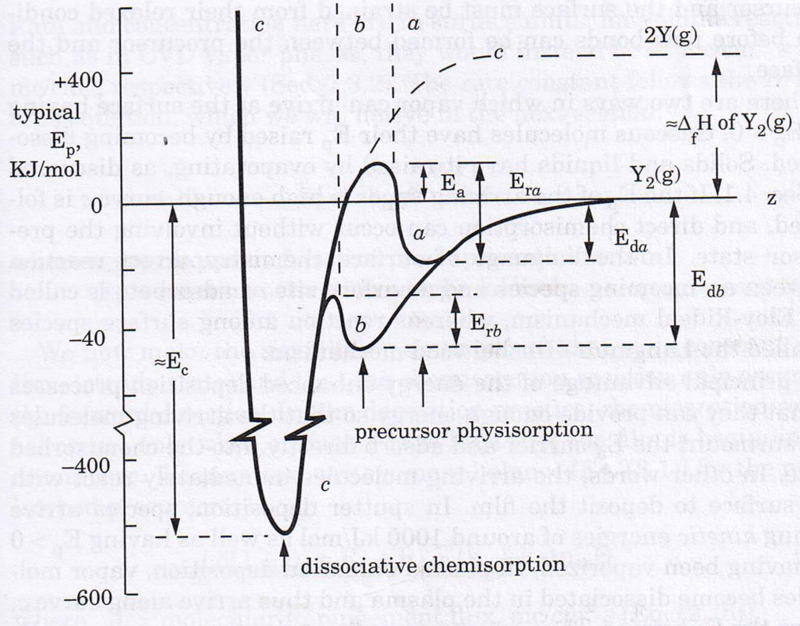


Figure 5.2 Energetics of the precursor adsorption model. Energy scale is typical only.

5.2. Surface Diffusion (Fig. 5.4)

Our discussion below will be based on the absolute-reaction-rate theory.

Rate equation….the rate of adatoms diffuse across (in the direction perpendicular to) a line of unit length on the surface

$$R_s = J_s / a(mc/cm^2 \bullet s)$$

where R_s is the rate of adatoms in the transition state per unit area make a jump of a distance a across a barrier E_s.

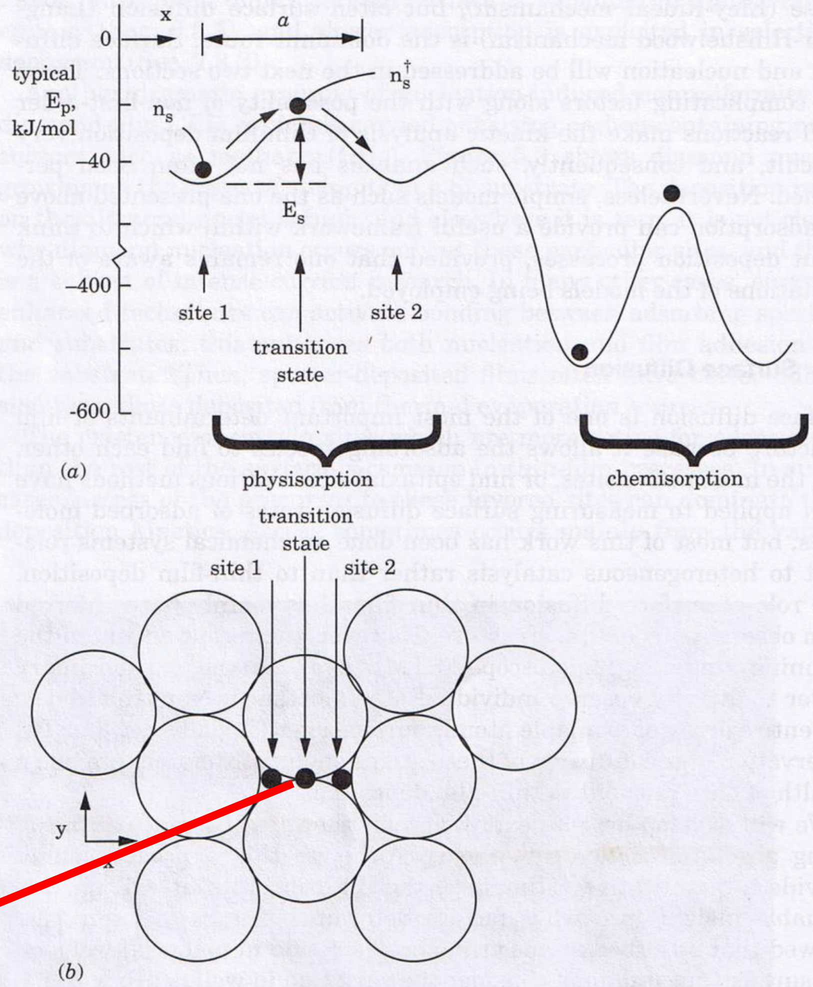
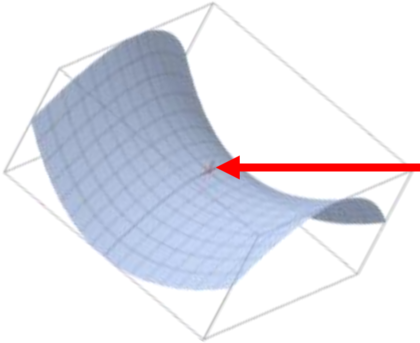
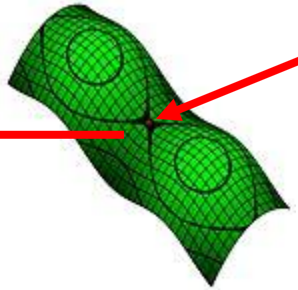


Figure 5.4 Surface diffusion: (a) potential energy vs. position x along the surface, and (b) typical adsorption sites on a surface lattice.





Use J_i in the 3-D case for J_s with only a change of the dimensionality of the atom concentration from #/cm^3 to #/cm^2:

$$J_s = \frac{1}{4} n_{st} \bar{c} = n_{st} \sqrt{\frac{k_B T}{2\pi m}}$$

from Chapter 2 where n_{st} is the surface concentration of adsorbates (in the unit of molecules per unit area) sitting at transition sites, i.e. those with sufficient energy to scale the diffusion barrier. Here, ĉ is used without proving its applicability to the 2D case. It turns out that rigorous derivation gives similar results.

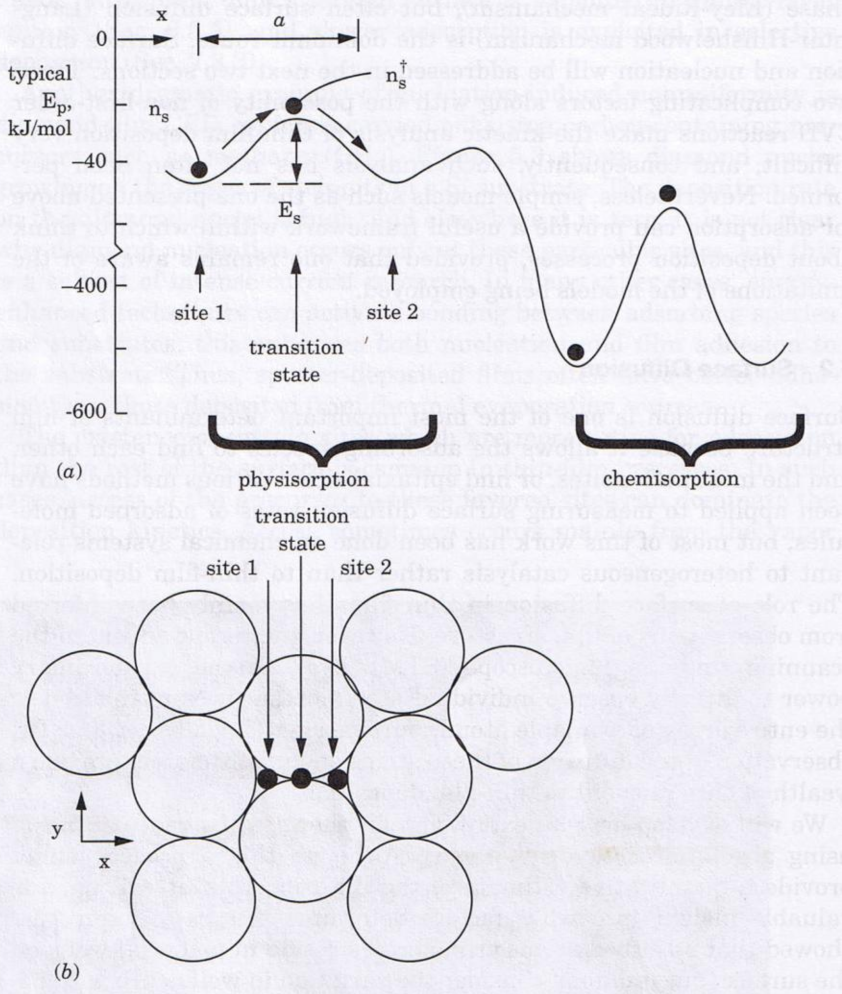


Figure 5.4 Surface diffusion: (a) potential energy vs. position x along the surface, and (b) typical adsorption sites on a surface lattice.

5.2.1. Recall the general expression of a first order chemical reaction given in eq.5.1 ($R_s=n_sk_s$) and combine it with the expression of $R_s=J_s/a$, we have:

$$R_s = \frac{n_{st}}{a}\sqrt{\frac{kT}{2\pi m}} = n_s\left(\frac{k_BT}{h}\right)e^{-E_s/RT} = n_s v_{os} e^{-E_s/RT} = n_s k_s$$

This is the main result of the absolute-reaction-rate theory. R_s is the total number of “hops” by all adsorbates to their neighboring sites. It is a first-order process.

The rate constant, k_s (the proportional constant relating R_s to n_s), represents the frequency of individual adsorbate “hops” to an adjacent site. Finally, ν_{0s} is not associated with a particular motion of adatoms contrary to many believes.

At 960 K;

$$\nu_{os} = \frac{k_B T}{h} \approx 2x10^{13} s^{-1}$$

In practice when all kinds of surfaces and the interaction between the adatoms and the surfaces are considered, ν_{0s} ~10^{13} – 10^{16} s^{-1}.

5.2.2. Corrugation ratio

We need a 3-D image of the potential near the substrate surface: the potential rises away from the surface along the surface norm, in the mean time, the potential oscillates along the surface with $E_s < E_d$ (compare Figs. 5.2 and 5.4).

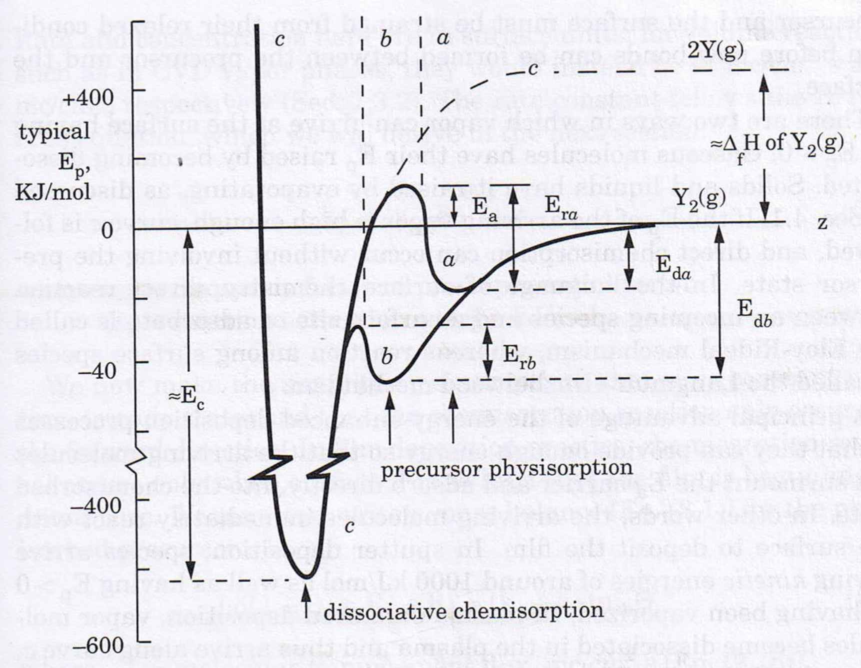


Figure 5.2 Energetics of the precursor adsorption model. Energy scale is typical only.

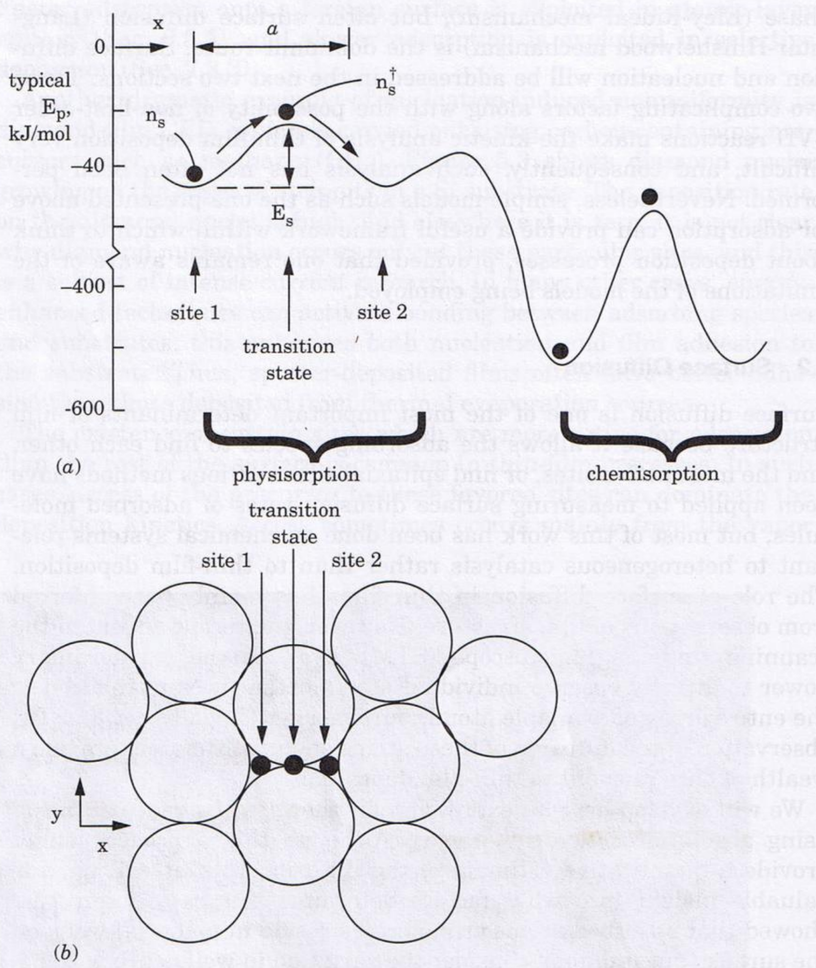


Figure 5.4 Surface diffusion: (*a*) potential energy vs. position x along the surface, and (*b*) typical adsorption sites on a surface lattice.

5.2.3. Mass-Migration….Surface diffusion

The characteristic distance a well-defined “patch” of adsorbates spreads out along the substrate surface.

We derive this using our knowledge of the hopping distance, *a*, of a single atom/molecule on the surface, and hopping frequency, k_s, and treat it as a “random walk” process. From statistics, we know the standard deviation of a Gaussian distribution is

$$\sigma = r\sqrt{N}$$

where r is the hopping distance and N is the number of hops within a given time period.

We use σ to <u>approximate</u> the mass migration length, Λ:

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

Recall k_s is the frequency of hopping.

5.2.3. Mass-Migration….Surface diffusion

To get a numerical idea, let’s assume a substrate temperature of 960 K, and a weak bonding of 20 kJ/mol for the adsorbates (recall from fig. 5.2 that E_d ranges from 20-40 kJ/mol):

$$k_s = \nu_{os} e^{-E_s / RT} = \frac{k_B T}{h} e^{-E_s / RT} \approx 1.6 \times 10^{12} s^{-1}$$

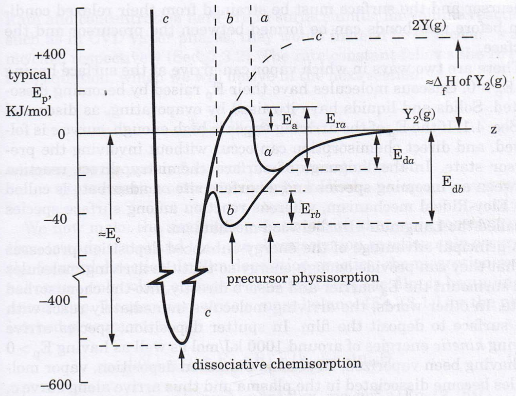


Figure 5.2 Energetics of the precursor adsorption model. Energy scale is typical only.

Assuming further that a = 0.3 nm, and t = 1 sec,

$$\Lambda \approx 380 \quad \mu m$$

Λ decreases with increasing E_s and decreasing T. For a strong bonding of 200 kJ/mol, k_s~2.6×10^2 s^{-1}, then Λ~4.8 nm !!! A 80,000 times reduction in Λ for 10 times increase in E_s!!

Therefore, ad-molecule diffusion always dominates over ad-atom diffusion.

5.2.4. Two Regimes in Mass Migration that Dictates t, the time duration of hopping:

It depends on whether Λ is limited by **desorption** or **burial** of the adatoms.

Recall from the conservation of mass: $J_r = R_r + R_d$, we have $R_r >> R_d$ in the

burial case:

$$t = \frac{n_o}{J_r}; \qquad J_r = J_i \cdot \alpha_c \qquad and \qquad n_{s0} = n_0$$

This is the time it takes to cover the surface by one monolayer.

$$\therefore \Lambda = a\sqrt{k_s t} = a\sqrt{\nu_{os} e^{-E_S/RT} \bullet \frac{n_o}{J_r}} = a\sqrt{\frac{\nu_{os} n_o}{J_r}}\, e^{-\frac{E_s}{2RT}}$$

Λ increases with increasing T;

J_r is the deposition flux.

5.2.4. Two Regimes in Mass Migration that Dictates t, the time duration of hopping:

In the **desorption case** which happens at high substrate temperatures when significant evaporation of the substrate material starts happening, we have the general form of temperature dependence:

$$R_d >> R_r$$

$$t = \frac{1}{k_c} = \frac{1}{v_{oc}} e^{E_c / RT}$$

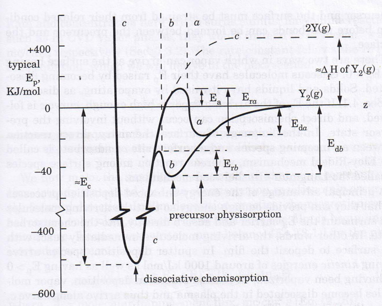


Figure 5.2 Energetics of the precursor adsorption model. Energy scale is typical only.

where we've made the simplified assumption of considering only the chemisorbed atoms with the corresponding E_c (fig) being the energy barrier for desorption while in reality the process is much more complex. This is because that adatoms and adsorbed molecules all can desorb each with different activation energy. Nonetheless, the general form of temperature dependence remains the same, with E_c replaced by another energy value.

$$\because E_c > E_s \qquad \therefore \Lambda = a\sqrt{k_s t} = a\sqrt{k_s / k_c} = a\sqrt{\frac{v_{os}}{v_{oc}} e^{(E_c - E_s)/2RT}}$$

in general as mentioned before, we have **Λ decreases with increasing T**.

5.2.4. Two Regimes in Mass Migration that Dictates t, the time duration of hopping:

1. Burial case: molecular flux limited growth regime:

$$\Lambda = a\sqrt{\frac{\nu_{os} n_o}{J_r}}\, e^{-\frac{E_s}{2RT}}$$

2. Desorption case: molecular flux limited growth regime:

$$\Lambda = a\sqrt{\frac{\nu_{os}}{\nu_{oc}}}\, e^{(E_c - E_s)/2RT}$$

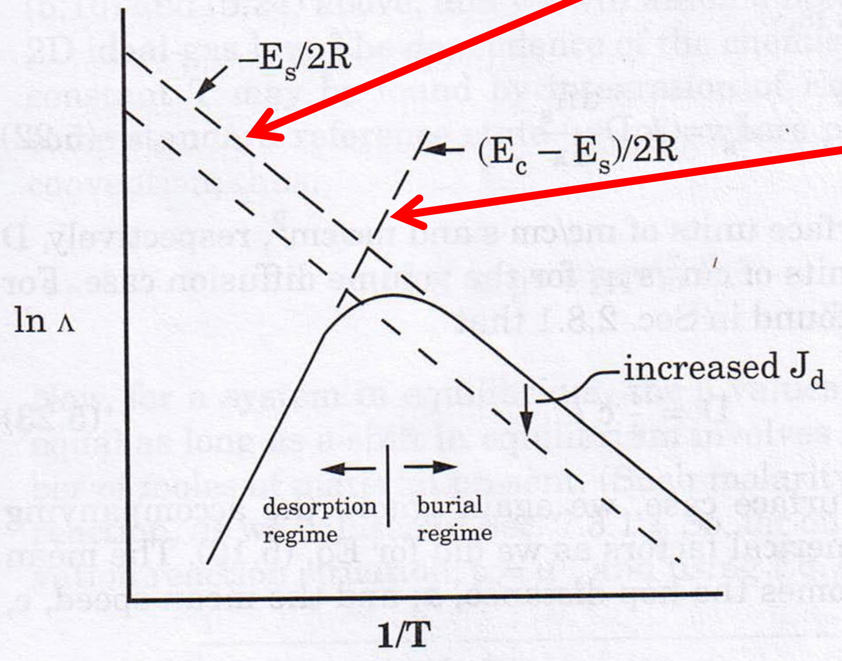


Figure 5.5 Behavior of surface diffusion length, Λ, with substrate T.

5.3. Nucleation

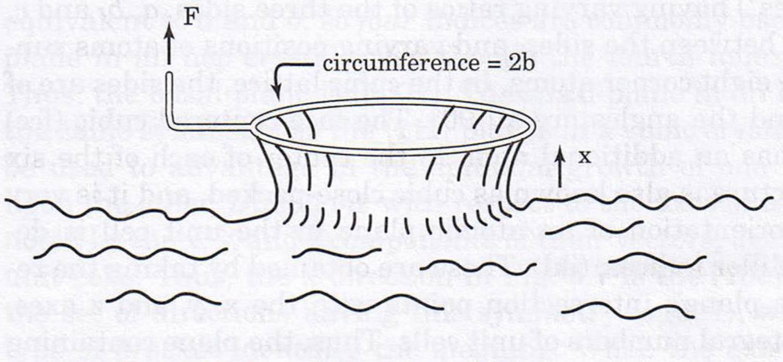


Figure 5.6 Surface tension of a liquid membrane.

5.3.1. Surface energy

Surface tension γ (N/m) is the force required to support the membrane per unit width of the membrane (see Fig. 5.6).

Be sure to include both surfaces of a given membrane.

Now consider the work needed (and therefore the energy increase) to create new surface area in the given setup:

$$\mathrm{F}\Delta x = 2b\gamma \bullet \Delta x$$

where b is the length of the circumference.

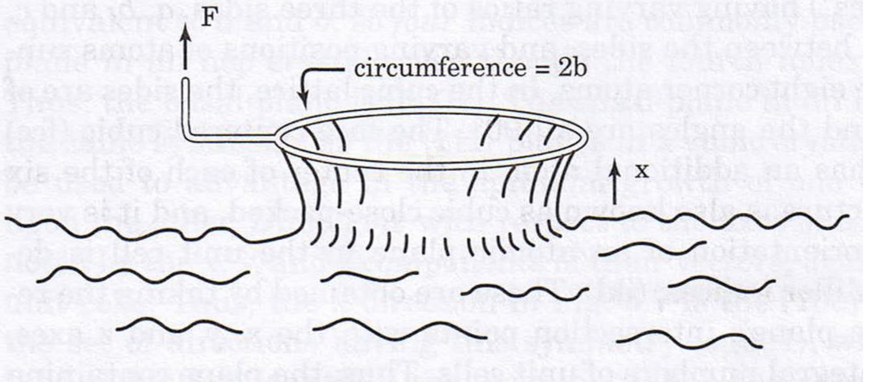


Figure 5.6 Surface tension of a liquid membrane.

∴ the new surface area created is $A = 2b\Delta x$

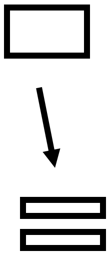
Since the work is stored in the form of surface energy, we can define the surface energy as the energy per unit area:

$$\frac{\mathrm{F}\Delta x}{A} = \frac{2b\gamma\Delta x}{2b\Delta x} = \gamma$$

γ has the dimension of energy per unit area, which is the same as force per unit length.

5.3.1. Surface energy (cont'd)

- The origin of the surface energy is the interatomic attraction. Atoms like to stay next to each other. Creating surfaces involves breaking of the bonds, and thus involves energy input.
- Understanding the physical origin of surface energy from theoretical modeling perspective:
  - For a given number of atoms forming the (typically rectangular shaped) crystal, let the atoms relax into their respective position so that the total energy of the collection of atoms is minimized;
  - Slice the slab of crystal in half, thereby creating an additional pair of surfaces and resulting in two smaller slabs;
  - Let the atoms in the two slabs relax to their respective position such that the energy of the two slabs reaches minimum.



  - The difference in the total energy of the system between the one slab and the two slabs case is two times the surface energy which is positive although the total energy is negative;

5.3.1. Surface energy (cont'd)

- γ is typically isotropic for liquid surfaces, and anisotropic for crystalline surfaces.
- Surface reconstruction lowers the actual surface energy comparing to an "ideal" surface because of the reduction in dangling bond density.
- Surface passivation also lowers the surface energy.
- The same concept that defines surface energy can be used for defining interface energy.
- Strong interaction or bonding between a thin film and a substrate corresponding to low interface energy γ_i.

5.3.2. The interplay of γ's. and the corresponding film growth modes (see Fig. 5.8)

$$\gamma_f + \gamma_i < \gamma_s$$

leads to layer by layer growth

(Frank - Van der Merwe).

- If the bonding between the film and the substrate is weak, then γ_i is high. In the extreme case of no bonding at all, γ_i becomes the sum of two separated surfaces, i.e.,

$$\gamma_i = \gamma_f + \gamma_s$$

$$\therefore \gamma_f + \gamma_i = 2\gamma_f + \gamma_s > \gamma_s \text{ always}$$

This leads to three-dimensional growths

(Vomer-Weber)

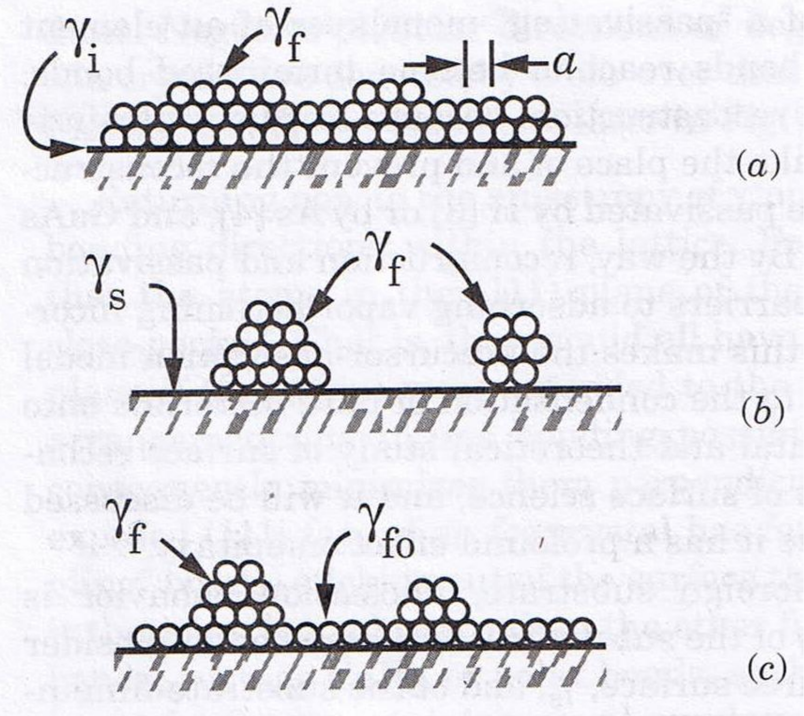


Figure 5.8 Film growth modes: (*a*) Frank-Van der Merwe (layer), (*b*) Volmer-Weber (island), and (*c*) Stranski-Krastanov.

- The third case happens when the film is under strain. In this case the surface energy consideration forces the first couple of monolayer to deposit layer-by-layer, followed by island growths to relief bulk strain (Stranski-Krastanov).

5.3.3. Interface Energy and Bonding

There are three types of bonding: ionic, covalent, and metallic, with the last one having the least directionality.

In general, interfacial bonding is stronger between same type of bonding.

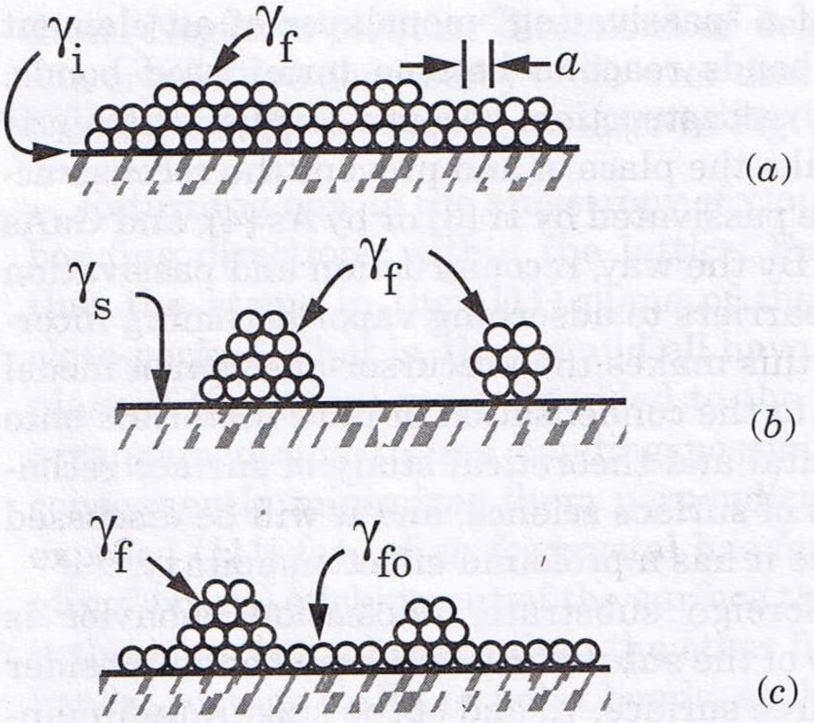


Figure 5.8 Film growth modes: (*a*) Frank-Van der Merwe (layer), (*b*) Volmer-Weber (island), and (*c*) Stranski-Krastanov.

5.3.4. Three-Dimensional (3-D) Nucleation (i.e. film formation ***via Vomer-Weber growth mode***)

3-D nucleation based on surface energy minimization (Fig. 5.9). Consider single component system for simplicity;

We know: $d\Delta G_m = \Delta V_m dp - \Delta S_m dT$, where Δ represents the difference between the vapor state and the condensed state, and $G_m = \mu$ by definition.

$$\therefore \frac{\partial \Delta G_m}{\partial p} = \frac{\partial \Delta \mu}{\partial p} = \Delta V_m \approx V_m = \frac{RT}{p}$$

Integrate from p_v to p (the deposition pressure), we get:

$$\therefore \Delta\mu = \mu_v - \mu_c = RT\ \ell n \frac{p}{p_v} = RT\ \ell n \frac{J_c}{J_v}$$

where we used,

$$J_i = \frac{N_A p}{\sqrt{2\pi MRT}}$$

$$J_v = \alpha_v J_{v0}$$

$$J_c = \alpha_c J_i$$

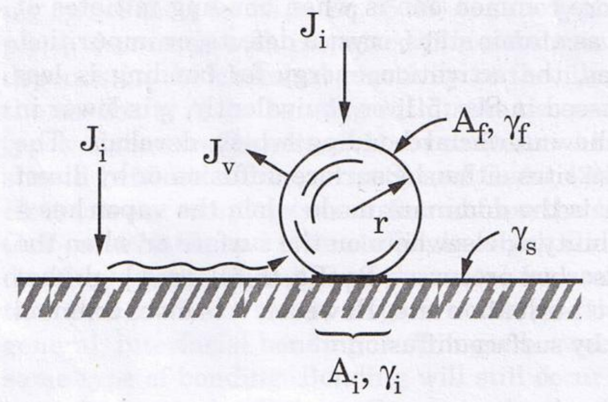


Figure 5.9 Geometry of condensate nucleus formation on nonwetting substrate.

and the assumption of a near equilibrium condition with $\alpha_c = \alpha_v$

$$\therefore \Delta\mu = \mu_v - \mu_c = RT\,\ell n\frac{p}{p_v} = RT\,\ell n\frac{J_c}{J_v}$$

- In equilibrium, we have: $\mu_v - \mu_c = 0$.

- If p (the actual vapor pressure) > p_v (the equilibrium vapor pressures) we have ***<u>super-saturation</u>***:

$$\frac{p}{p_v} = \frac{J_c}{J_v} > 1$$

i.e. $\mu_v > \mu_c$, and condensation occurs (at the substrate side).

- If on the other hand $p < p_v$ we have ***<u>under-saturation</u>***:

$$\frac{p}{p_v} = \frac{J_c}{J_v} < 1$$

i.e. $\mu_v < \mu_c$, and vaporization occurs (at the source side).

Because μ is defined as G per unit mole in a single component system, thus $\mu = G_m$.

The G change per nucleus (**not per mole**) during condensation from vapor into solid or liquid is:

$$\Delta G = -(\Delta\mu \times \# \text{ of moles}) + \text{surface energy}$$

where $\frac{V}{V_{mc}}$ is the number of moles in the nucleus, γ_f is the surface tension of the nucleus and A_f is the surface area of the nucleus.

Here we have assumed that the wetting of the substrate is poor, therefore $A_i << A_f$, and consequently, $\gamma_i A_i$ can be neglected comparing to $\gamma_f A_f$.

$$\therefore \Delta G = -(\mu_v - \mu_c)\frac{V}{V_{mc}} + \gamma_f A_f$$

Note: the reason for the addition of surface energy is not because the cluster has higher surface energy compared to atoms in vapor phase, instead it is to account for the fraction of the atoms on the surface of the nucleus that is not covered by the bulk property in the first term.

Using Eq. 5.37:

$$\Delta G = -\left(RT \ln \frac{p}{p_v} \right) \bullet \frac{\frac{4}{3}\pi r^3}{V_{mc}} + \gamma_f \cdot 4\pi r^2$$

$\therefore \Delta G$ increases with r, going through a maximum, and then decreases.

At ΔG_{max}, we have: $$\frac{d(\Delta G)}{dr} = 0$$

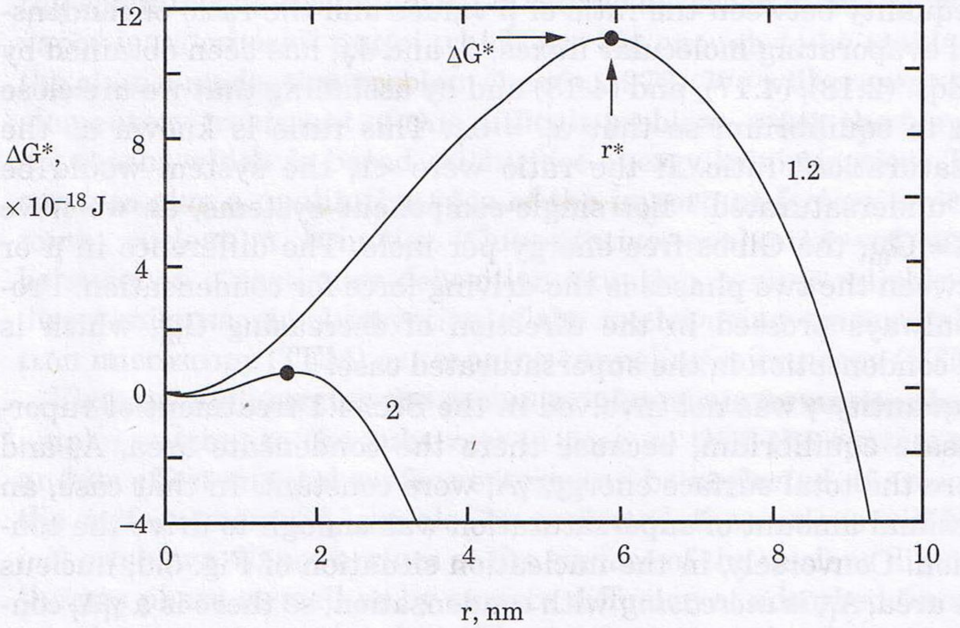


Figure 5.10 Classical nucleation behavior of water for two values of the supersaturation ratio (• denotes critical-cluster condition).

Start with:

$$\Delta G = -\left(RT\ln\frac{p}{p_v}\right)\bullet\frac{\frac{4}{3}\pi r^3}{V_{mc}} + \gamma_f \cdot 4\pi r^2$$

Carrying out the derivative and let $\frac{d(\Delta G)}{dr} = 0$, we get:

$$\Delta G^* = \frac{(16/3)\pi\gamma_f^{\,3}}{\left[\left(\frac{RT}{V_{mc}}\right)\ln\left(\frac{p}{p_v}\right)\right]^2}$$

and

$$r^* = \frac{2\gamma_f}{\left(\frac{RT}{V_{mc}}\right)\ell n\left(\frac{p}{p_v}\right)}$$

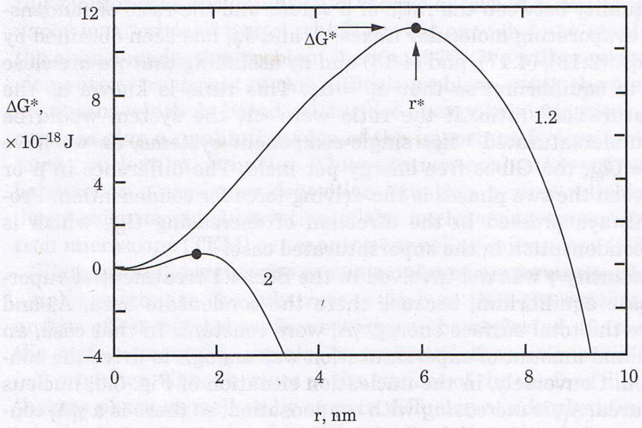


Figure 5.10 Classical nucleation behavior of water for two values of the supersaturation ratio (• denotes critical-cluster condition).

where r* is the critical nucleus radius (see Fig. 5.10).

This is the trend of r^2 vs. r^3. For r > r*, the nucleus grows, and for r < r*, the nucleus shrinks.

Comparison between the two curves also shows the importance of p/p_v.

Some observations of ΔG^*:

- It decreases with increasing p/p_v;
- It decreases with decreasing surface energy, γ_f ; the influence of γ_f on ΔG^* is much more than p because of the logarithmic function. However, γ_f is typically not a tunable parameter but p is.

In Vomer Weber growth mode, film forms through coalescence of growing nuclei.

5.3.4.1. Kinetics vs. Thermodynamics

It is important to have a good idea of whether a process on hand is approaching equilibrium or is limited by kinetics.

Approach to equilibrium requires the forward and reverse rates to be fast enough so that they become balanced within the applicable time scale, which may be the time for deposition of one monolayer.

In Vomer-Weber growth mode, smooth film can also be obtained by limiting the surface diffusion of adatoms.

5.3.4.2. Other Complications

5.3.4.2.1. Heterogeneous vs. homogeneous nucleation.
n* could be determined by the available heterogeneous nucleation sites.

5.3.4.2.2. The discrete nature of typical surfaces becomes dependent on whether the surface is convex or concave, and the details of the surface termination.

5.4.4.2.3. Facets and **Wulff theorem**
Various facets have different γ (see fig.5.11)
When the surface energy is minimized, Wulff theorem states:

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

i.e., the higher the surface energy of a particular facet, the further away from the center of the nucleus it is. This comes out of the condition of surface energy minimization:

$$\sum_k \gamma_k \bullet A_k = \text{minimum}$$

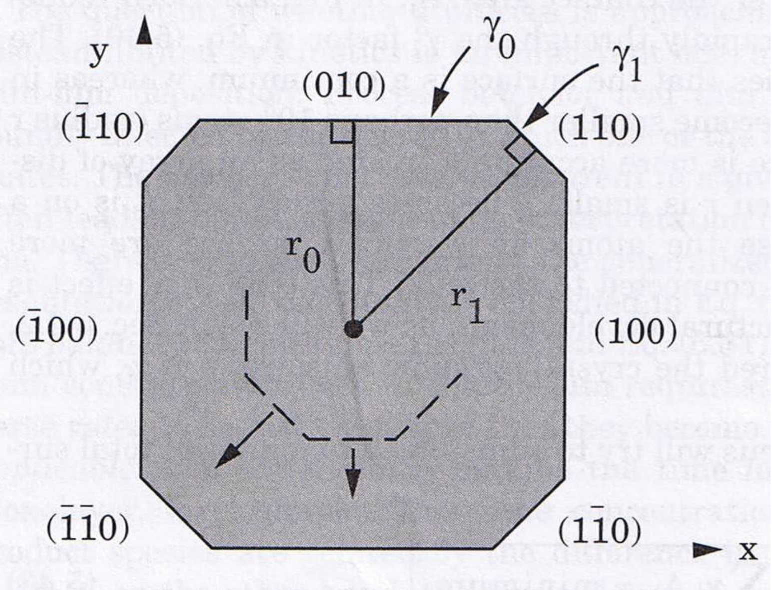


Figure 5.11 Wulff construction for a needle crystallite oriented along the z axis (perpendicular to the paper).

5.3.4.3. Young’s equation for liquid or molten films with isotropic γ

Force balance in the horizontal direction at the edge of a nucleus can be written in terms of the surface energies because the γ’s are also the force per unit length acting on the edge of interest as discussed at the beginning of Section 5.3. The condition of force balance of the edge of a liquid droplet can thus be visualized from the following schematic:

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

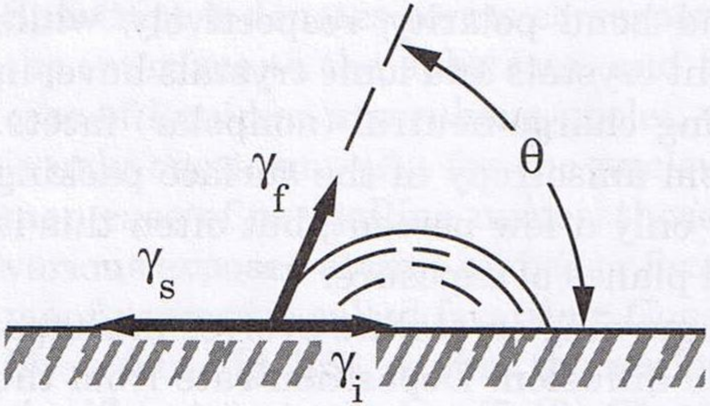


Figure 5.12 Wetting angle of a liquid nucleus.

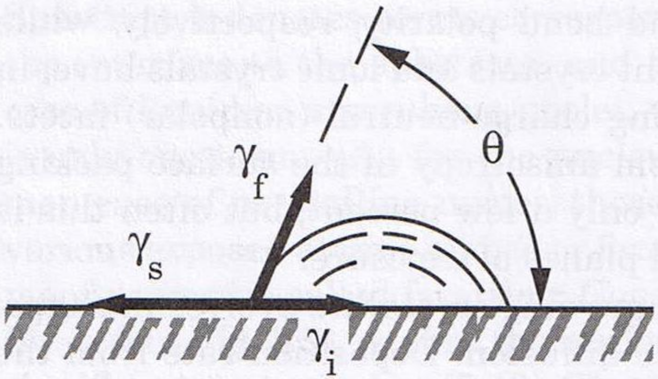


Figure 5.12 Wetting angle of a liquid nucleus.

θ, which is known as the wetting angle increases when γ_s decreases relative to γ_i for a fixed γ_f i.e., from good to poor wetting.

It is a fact that small nuclei are likely to be molten at substrate T above 2/3 of the absolute melting T of the film material in the bulk form.

Note the direction of the force associated with the surface tensions are defined as:

$$F = -\frac{\partial G}{\partial x}$$

i.e. the force is in the direction of reducing surface area .

In the case of very small contact angle θ, i.e., no 3-D nucleation tendency, 2-D nucleation happens, i.e. we are in ***Frank-van der Merwe growth mode***. This is because an adatom alone has higher energy than when it is bond to other surface atoms.

The collection of surface adatoms can be viewed as 2-D gases. If we define the adatom density n_v for which its μ is the same as the atoms incorporated on a straight edge of a surface terrace as the 2-D saturation vapor concentration, then the super-saturation ratio becomes:

$$\frac{n_s}{n_v}$$

where n_s is the actual density in gas phase, i.e. surface monomer adatoms not incorporated in any 2D terrace.

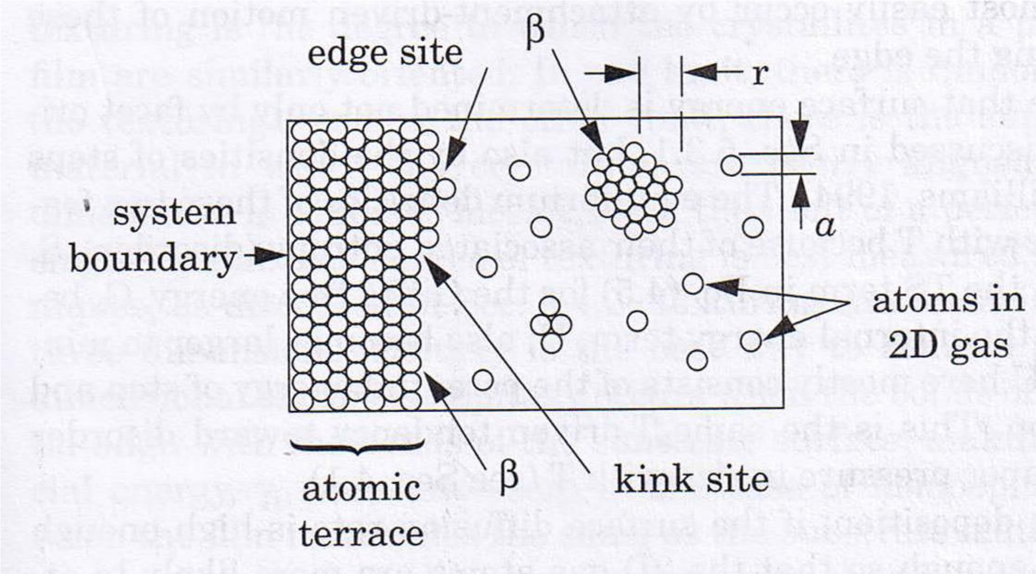


Figure 5.13 Geometry of 3D nucleation, looking down at the surface.

5.3.5. Two-Dimensional (2-D) Nucleation (fig 5.13)
(i.e. film formation via ***Frank-van der Merwe mode***)

Following similar argument as in 3-D case, we get:

$$r^* = \frac{\beta}{a\left(\frac{RT}{V_{mc}}\right)\ell n\left(\frac{n_s}{n_v}\right)} \qquad and \qquad \Delta G^* = \frac{\pi\beta^2}{a\left(\frac{RT}{V_{mc}}\right)\ell n\left(\frac{n_s}{n_v}\right)}$$

where β is the edge energy, in analogy to the surface energy in 3-D case, a is the monolayer thickness.

The coalescence of these 2-D terraces forms a continuous film.

In analogy to heterogenous nucleation sites, kink-sites on a single crystal surface is energetically favored site for adatoms to attach to.

There are two modes for 2-D terrace development:

- $\Lambda < L$ leads to island nucleation and coalescence.
- $\Lambda > L$ leads to step edge propagation where L is the average separation between steps.

At the surface, we have the structure shown in fig.5.23. At the location where a grain boundary intersects the film surface, there is a cusp known as "thermal groove". The origin is the weaker bonding along grain boundaries leading to an interface energy γ_i. From the consideration of force balance, we need to have the sum of the vertical components of γ_1 and γ_2 counter balance γ_i, and the horizontal components of γ_1 and γ_2 balancing out one another, i.e. $\gamma_1\cos\theta_1 = \gamma_2\cos\theta_2$. For $\theta_1 > \theta_2$, we must have $\gamma_1 > \gamma_2$.

The difference in γ implies a difference in the chemical potential. Surface diffusion proceeds in the direction of lower μ, i.e. from column 1 to column 2. Qualitatively, the relationship between the surface curvature and the associated chemical potential can be shown below: (See Fig. 5.24 & the next slide)

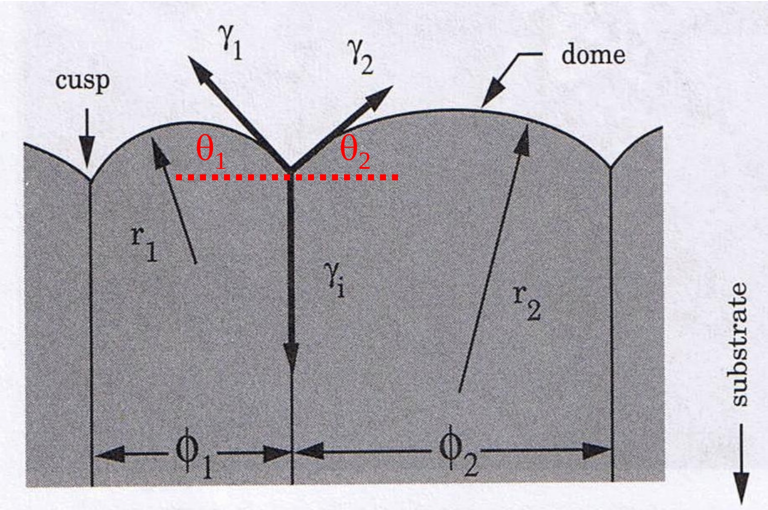


Figure 5.23 Geometry and surface energetics of columnar grain growth.

5.4.5. Amorphous Films

Grain boundaries: the weak links in a material, and the high mobility diffusion paths. See Fig. 5.26 for impurity diffusion through a single crystal and a poly-crystal sample.

Diffusion: at low and moderate T_s, grain boundary diffusion dominates, and at high T_s bulk diffusion dominates because of the higher activation energy.

Amorphous film can be used to reduce the impact of grain boundaries by minimizing the size of them.

Amorphous films can re-crystallize upon annealing. This is especially true for metals because of the non-directional nature of the metallic bonding. Some metal crystallize at cryogenic temperatures!!

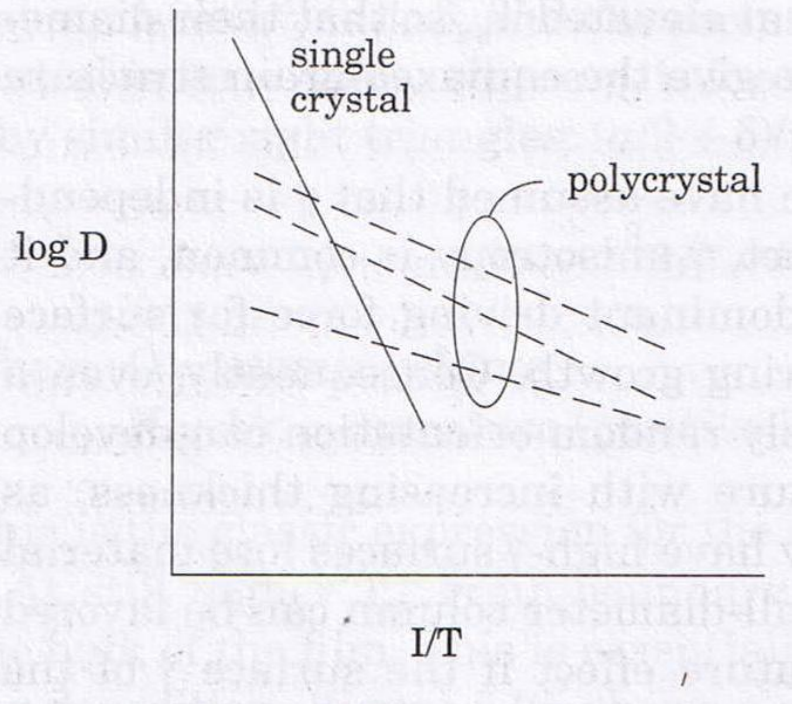


Figure 5.26 Typical diffusion behavior in a polycrystalline solid. D = diffusivity.

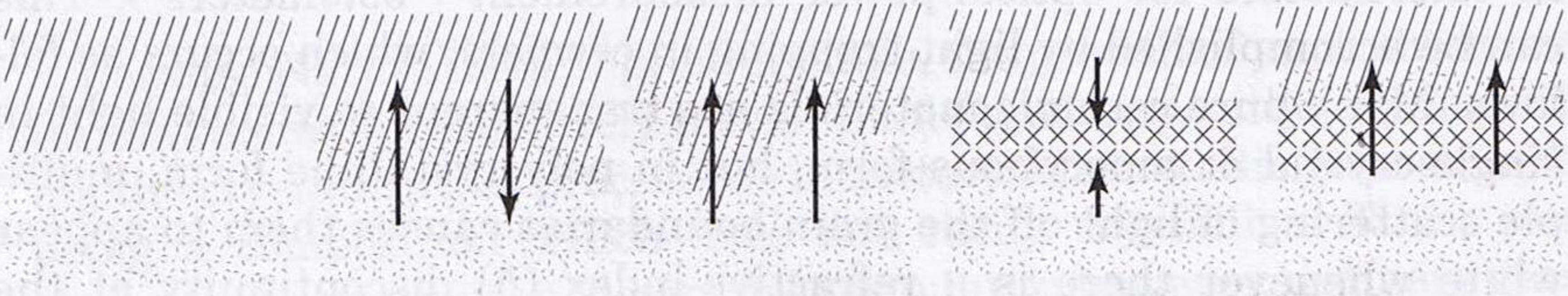
One way to minimize recrystallization is by mixing in materials with distinctively different lattice constant or symmetry for the purpose of immobilizing the grain boundaries, as in the case of metallic glass.

The normal glass we use also contains elements such as Pb to prevent the SiO_2 from going through devitrification, i.e. turning into quartz. Because Pb does not fit into the matrix of quartz, its presence serves the purpose.

Amorphous to single crystal is a continuous coarsening of the size of the crystallites.

5.5. Interfaces (Fig. 5.27—several types)

- Formed during deposition while the interface is forming (surface diffusion/segregation) and afterwards via solid diffusion.
- The specific behavior of interface inter-diffusion is hard to predict because of the strong dependence on many factors, including materials combination, temperature cycles.

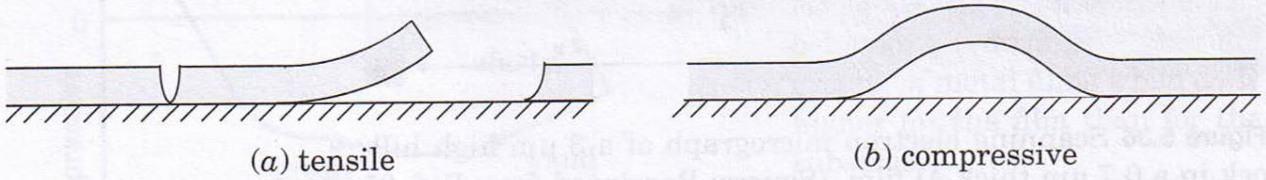


(*a*) abrupt (*b*) diffused (*c*) pitted (*d*) reacted (*e*) voided

Figure 5.27 Interface types. (Arrows indicate direction of diffusion.)

5.6.2. Problems

- Films crack under tensile stress and then peel off starting from the stress concentration points.
- Films buckle up under compressive stress. (fig 5.35)



(*a*) tensile (*b*) compressive

Figure 5.35 Catastrophic failure from film stress.