F4280 Technology of thin film deposition and surface treatment
3. Evaporation

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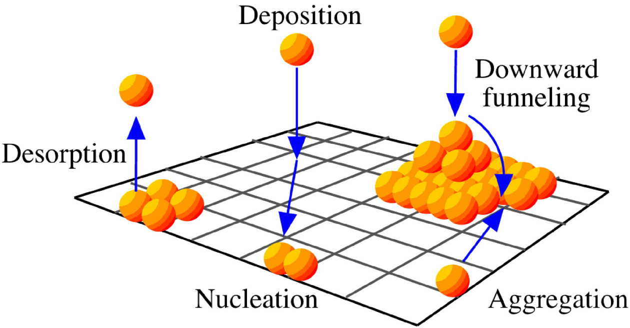
Outline - chapter 4. Deposition

- 4. Deposition

4.1 Introduction to Deposition

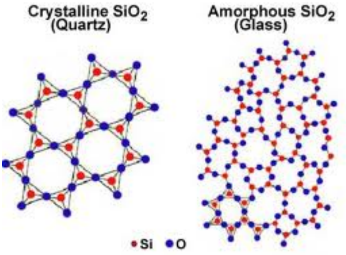
Deposition may be considered as six sequential substeps:

1. **Adsorption** of arriving atoms and molecules on the surface.
2. **Diffusion** before becoming incorporated into the film.
3. **Reaction** of adsorbed species with each other and the surface to form the bonds of the film material.
4. Initial aggregation of the film material - **nucleation**.
5. Development of a structure (**morphology**) as the film grows thicker. It includes topography (roughness) and crystallography.
6. **Diffusional interactions** within the bulk of the film and with the substrate



4.1 Introduction to Deposition

Film crystallography may range from amorphous ⇒ polycrystalline ⇒ single-crystal.



Single-crystalline films are obtained by **epitaxy**, i.e. replication of the crystalline order of a single-crystal substrate

- homoepitaxy
- heteroepitaxy

In this chapter, we will consider that only **thermal energy** is being supplied to the surface except where energy enhancement is specifically noted. Adding energy by **nonthermal means** is an important process technique used in **energy beams and plasma processes**.

4.2 Chemical Reactions - Reaction Rate

Chemické reakce mohou zahrnovat reakce mezi plyny, kapalinami nebo pevnými látkami. Reakce se nazývá **homogenní**, pokud jsou reaktanty ve stejném skupenství a **heterogenní** pokud jsou reaktanty z dvou nebo více různých skupenství. Reakce probíhající na povrchu katalyzátoru jsou také považovány za heterogenní. Tudíž reakce mezi dvěma tekutinami je homogenní, zatímco reakce mezi plynem a pevnou látkou je heterogenní.
Uvažujme reakci

$$aA + bB \cdots \longrightarrow qQ + sS \ldots \tag{1}$$

Lze napsat, že A a B reagují rychlostí

$$r'_A = -\frac{\mathrm{d}N_A}{\mathrm{d}t} \quad r'_B = -\frac{\mathrm{d}N_B}{\mathrm{d}t} \tag{2}$$

a Q a S se vytvářejí rychlostí

$$r'_S = \frac{\mathrm{d}N_S}{\mathrm{d}t} \quad r'_Q = \frac{\mathrm{d}N_Q}{\mathrm{d}t}, \tag{3}$$

kde N_j reprezentuje molární množství reakční složky (v kilomolech) a t je čas.

4.2 Chemical Reactions - Reaction Rate

Mezi reakčními rychlostmi existují tyto vztahy

$$r' = -\frac{1}{a}\frac{\mathrm{d}N_A}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}N_B}{\mathrm{d}t} = \frac{1}{q}\frac{\mathrm{d}N_Q}{\mathrm{d}t} = \frac{1}{s}\frac{\mathrm{d}N_S}{\mathrm{d}t}. \tag{4}$$

Přičemž každou část této rovnice lze považovat za **reakční rychlost**. Toto lze zobecnit na případ N chemických látek j, které se účastní M nezávislých chemických reakcí i.

$$\alpha_{i1}A_1 + \alpha_{i2}A_2 + \cdots + \alpha_{iN}A_N = 0, \quad \text{tj.} \quad \sum_{j=1}^{N} \alpha_{ij}A_j = 0 \quad i = 1, 2, \ldots M \tag{5}$$

Používáme konvenci, že stechiometrické koeficienty α_{ij} bereme jako *kladné pro produkty a jako záporné pro reaktanty*.

Reakční rychlost je obecně vztažena k nějakému množství, například objemu. Když V reprezentuje objem, který zabírá reakční směs, pak

$$r_i = \frac{1}{V}\frac{1}{\alpha_{ij}}\left(\frac{dN_j}{\mathrm{d}t}\right)_i. \tag{6}$$

Pokud se objem reakční směsi nemění

$$r_i = \frac{1}{\alpha_{ij}}\frac{\mathrm{d}C_j}{\mathrm{d}t}. \tag{7}$$

V tomto případě by pro získání reakční rychlosti stačilo měření koncentrace.

4.3 Conversion and Extent of Reaction

Často se místo koncentrací v rovnicích užívá pojem **konverze**:

$$x'_A = N_{A0} - N_A \quad x'_B = N_{B0} - N_B \tag{8}$$

nebo pro konstantní objem,

$$x''_A = C_{A0} - C_A \quad x''_B = C_{B0} - C_B. \tag{9}$$

Dolní index 0 označuje počáteční množství chemické látky.

Nejčastěji se setkáváme s pojmem **relativní konverze**

$$x_A = \frac{N_{A0} - N_A}{N_{A0}}, \quad x_B = \frac{N_{B0} - N_B}{N_{B0}}, \tag{10}$$

která nám říká, jak daleko reakce postoupila.

4.3 Stupeň rozvoje reakce, Maximální rozsah reakce

Alternativní koncept ke konverzi je **stupeň rozvoje reakce**, který pro (5) definujeme

$$\xi = \frac{N_j - N_{j0}}{\alpha_j}. \tag{11}$$

Jde o množství, které je stejné pro jakoukoli chemickou látku. N_{j0} je počáteční množství A_j které se vyskytuje v reakční směsi. ⇒

$$N_j = N_{j0} + \alpha_j \xi \tag{12}$$

Pro vícenásobné reakce $i = 1, 2, \ldots M$ pak

$$N_j = N_{j0} + \sum_{i=1}^{M} \alpha_{ij} \xi_i. \tag{13}$$

Rovnice (10) a (12) mohou být zkombinovány a získáme

$$N_j = N_{j0} + \alpha_j \frac{N_{A0}}{a} x_A. \tag{14}$$

Jestliže látka *A* je limitující reaktant (zastoupen v nejmenším množství), pak **maximální rozsah reakce** najdeme pomocí

$$0 = N_{A0} + \alpha_A \xi_{\max} \tag{15}$$

a relativní konverze definovaná v rovnici (10) přechází na

$$x_A = \frac{\xi}{\xi_{\max}}. \tag{16}$$

4.4 Rate Constant, Order of Reaction

Na základě experimentálních pozorování (později vysvětleno pomocí kolizní teorie) bylo zjištěno, že rychlost reakce $aA + bB \longrightarrow qQ + sS$ lze vyjádřit jako

$$r = k_c C_A^a C_B^b. \tag{17}$$

Člen k_c se nazývá **rychlostní konstanta**. Z definice je rychlostní konstanta nezávislá na množství jednotlivých reakčních látek, ale je závislá na jiných proměnných, které ovlivňují reakční rychlost.

Pokud je r vyjádřena v $\mathrm{kmol\,m^{-3}\,hr^{-1}}$, pak k_c má rozměr $(\mathrm{kmol\,m^{-3}})^{1-(a+b+\dots)}\ \ \mathrm{hr^{-1}}$

Parciální tlaky mohou být také použity k měření množství reakčních látek

$$r = k_p p_A^a p_B^b. \tag{18}$$

V tomto případě jsou pak rozměry rychlostní konstanty k_p $(\mathrm{kmol\,m^3})\ \ \mathrm{hr^{-1}}\ \mathrm{Pa}^{-(a+b+\dots)}$

V souladu s rovnicí ideálního plynu

$$C_i = \frac{p_i}{RT}, \tag{19}$$

takže

$$k_c = k_p (RT)^{a+b+\cdots}. \tag{20}$$

4.4 Rate Constant, Order of Reaction

Mocniny a, b, $\ldots$ se nazývají **parciální řády** reakce (1) $aA + bB \cdots \longrightarrow qQ + sS \ldots$

Součet $a + b + \ldots$ můžeme nazvat **celkovým řádem** nebo jen **řádem** reakce.

Ve skutečnosti by měly být řády v předchozích reakcích nahrazeny veličinami a', b', $\ldots$, které nejsou nezbytně nutně ve shodě (pouze pro jednoduché procesy) se stechiometrickými koeficienty a, b, $\ldots$ a', b', $\ldots$ musí být zjišťovány experimentálně. Pouze u jednoduchých reakcí je řád reakce 1, 2 nebo 3. V případě, že stechiometrická rovnice (1) je pouze obecnou rovnicí procesu, který zahrnuje několik kroků, tak nelze řád reakce určit na základě stechiometrických koeficientů.

Pro **nevratnou reakci prvního řádu při konstantním objemu** $A \longrightarrow Q$ máme

$$r_A = -\frac{dC_A}{dt} = kC_A. \tag{21}$$

Pokud tedy známe rychlostní konstanty k (hr^{-1}), tak z rovnice (21) můžeme spočítat reakční rychlost r_A pro jakoukoli koncentraci reakčních složek. A naopak pokud známe funkci změny koncentrace na čase (21), tak můžeme spočítat rychlostní koeficient. Toto je **diferenciální metoda pro získání rychlostní konstanty** k

Integrální metoda využije integrace rovnice (21), což dává

$$kt = ln\left(\frac{C_{A0}}{C_A}\right) \tag{22}$$

a semilogaritmický graf C_{A0}/C_A v závislosti na čase t nám také dává k.

4.4 Rate Constant, Order of Reaction

We showed relations for the rate constant of the irreversible 1st order reaction $A \rightarrow Q$.

Now, think about the expressions for

- reversible 1st order reaction $A \leftrightarrows^{1}_{2} Q$
- irreversible 2nd order reaction $2A \rightarrow Q + S$
- irreversible 2nd order reaction $A + B \rightarrow Q + S$

4.5 Complex Reactions

We can encounter also with **complex reactions**: parallel, consequtive, free radical chain reaction (initiation, propagation, termination), free radical addition

4.6 Arrhenius plot

The rate of reaction depends on the temperature through the variation of the rate coefficient k according to the **Arrhenius plot**

$$k = A_0 \exp\left(-E/RT\right) \tag{23}$$

where

- T is the temperature in K,
- E is the **activation energy** (J/mol),
- R is the gas constant (JK/mol),
- A_0 is a constant called the frequency factor.

Arrhenius came to this formula by thermodynamic considerations.

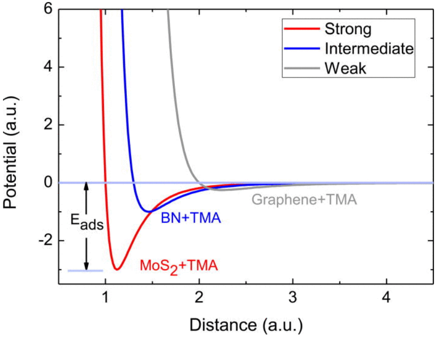
When $\ln k$ is plotted versus $1/T$, a straight line with the slope $-E/R$ is obtained

$$\ln k = -\frac{E}{R}\frac{1}{T} + \ln A_0. \tag{24}$$

4.7 Adsorption

Consider a molecule approaching a surface from the vapor phase.

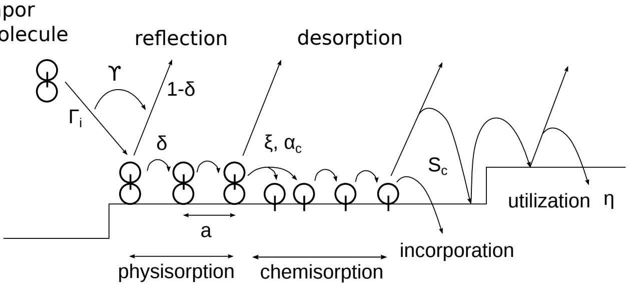
- **A few atomic distances from the surface** molecule begins to feel an attraction - interaction with the surface molecules by **van der Waals forces** (London dispersion forces):
  - molecules/atoms without dipole moments (symmetrical or intert) interact due to oscillating dipoles, i.e. induced-dipole interaction
  - polar molecules (permanent dipoles) interact more strongly
- The approaching molecule is **being attracted into a potential well** - accelerates down the curve until it passes the bottom and is **repelled by steeply rising potential**.



An illustrative Lennard-Jones potential model for physical adsorption.

Physisorption

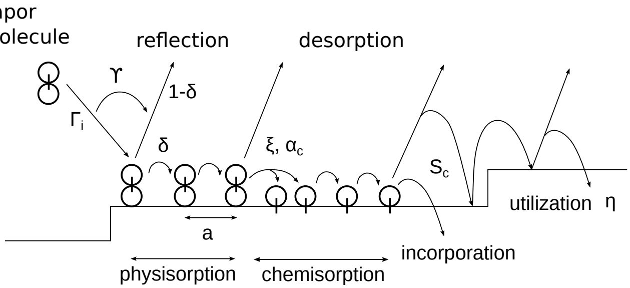
- If enough of the molecule's perpendicular component of momentum is dissipated into the surface the molecule cannot escape the well after being repelled ⇒ **physisorption**
  - fraction of physisorbed molecules - **trapping probability** δ
  - reflected $1-\delta$
  - δ is different from **thermal accomodation coefficient** γ introduced previously
  - molecule is at least partially accomodated thermally to the surface temperature T_s even when it is reflected
- The physisorbed molecule is mobile on the surface except at cryogenic T - **hopping** (**diffusing**) between surface atomic sites.



Chemisorption

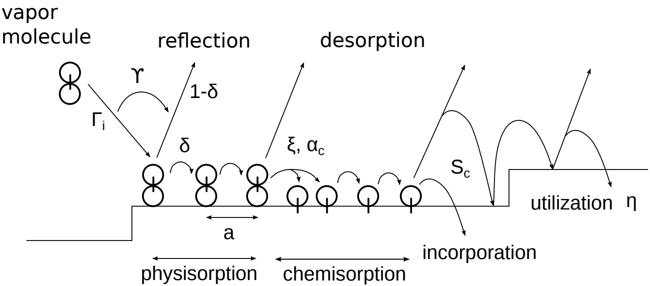
During surface diffusion the molecule

- may **desorb** after a while by gaining enough energy in the tail of the thermal energy distribution.
- may undergo a further interaction consisting of the formation of chemical bonds with the surface atoms, i. e. **chemisorption**. The **chemisorption reaction probability** ξ is used in the case of chemisorption on a foreign substrate instead of **condensation coefficient** α_c.
- some of adsorbed species eventually escape back into the vapor phase ⇒ **sticking coefficient** S_c - fraction of the arriving vapor that remains adsorbed for the duration of the experiment.



Chemisorption

- **Sticking coefficient S_c** has less fundamental meaning than δ and ξ (or α_c) that are determined solely by chemistry and energy. Nevertheless, S_c is very useful in thin film deposition - it is the fraction of arriving vapor incorporated into the film (buried before escaping).
- **Utilization fraction η** of a chemical vapor - fraction of molecules utilized for the deposition $\Rightarrow$ η can approach unity even when S_c is very low.



Precursor State

Chemisorption - sharing electrons, physisorption - dipole interaction.
If both adsorption states exist, the physisorption is called precursor state.
The precursor model may also be applied to cases where both the adsorption states involve chemical bonding but one is weaker.

The precursor model has long been applied to heterogeneous catalysis, thin-film deposition and condensation of molecular vapors. Some examples:

- In most CVD reactions, the feed vapors adsorb as molecules that undergo reaction breaking their molecular bonds and form new bonds to surface

$$\mathrm{SiH_4(g)} \rightarrow \cdots \rightarrow \mathrm{SiH_4(a)} \rightarrow \mathrm{Si(c)} + 2\mathrm{H_2(g)} \tag{25}$$

- In deposition of compounds from separate vapor sources of each element, adsorbing vapor bonds much more strongly to surface sites occupied by the other element

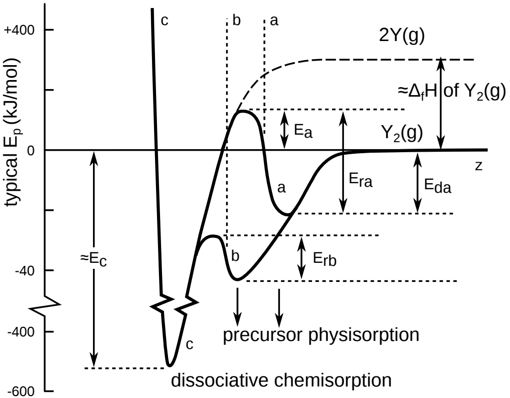
$$\mathrm{Zn(g)} + \mathrm{Se(a)} \rightarrow \mathrm{ZnSe(c)} \quad \text{and} \quad \mathrm{Se(g)} + \mathrm{Zn(a)} \rightarrow \mathrm{ZnSe(c)} \tag{26}$$

- Si chemically passivated by H reacts with adsorbates mainly at those few sites that are missing H atom. On the H-passivated sites, adsorbates remain only physisorbed.
- Atomically flat surfaces often bond more strongly with adsorbates at atomic steps.

Recent theory indicates that **even the condensation of monoatomic vapor such as Al can involve both adsorption states:** the precursor state = Al-Al dimer with limited bonding to bulk Al.

Energetics of Precursor Adsorption Model

Consider hypothetical diatomic gas-phase molecules Y_2(g) adsorbing and then dissociative chemisorbing as two Y atoms:

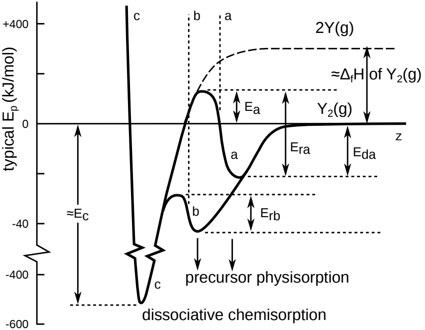


Lifting **atomic Y** out of its potential well along **curve c** results in much higher molar potential energy E_p in the gas phase - roughly the **heat of formation, $\Delta_f H$**, of $2Y$(g) from Y_2(g).

The **curve a** represents **activated chemisorption** - there is an activation energy E_a to be overcome for Y_2(g) to become dissociatively chemisorbed.

For deeper precursor well, **curve b**, chemisorption is not activated though there is still a barrier E_rb.

Eley-Ridel and Langmuir-Hinshelwood mechanisms



Two ways in which vapor can arrive at surface having $E_\mathrm{p} > 0$:

- Gaseous molecules have their E_p raised by becoming dissociated.
- Solids and liquids have it raised by evaporating.

Energy-enhanced deposition processes provide enough energy that $E_\mathrm{p} > E_\mathrm{a}$

- sputter deposition - arriving species have kinetic energy $\sim$ 1000 kJ/mol and $E_\mathrm{p} > 0$ (vaporized state).
- plasma-enhanced CVD - vapor molecules are dissociated in plasma

- If **curve c** is followed (E_p is high enough) direct chemisorption (without involving precursor state) $\Rightarrow$ **Eley-Rideal mechanism**, i.e. direct reaction between an incoming species and a surface site
- Contrary, reaction among surface species $\Rightarrow$ **Langmuir-Hinshelwood mechanisms**

Thermally controlled deposition process

In evaporation and CVD, the vapors often adsorb first into the precursor state (**curve a, b**)

- and chemisorb by overcoming the barrier $E_{\mathrm{r(a,b)}}$
- or desorb by overcoming the heat of physisorption $E_{\mathrm{d(a,b)}}$.

$\Rightarrow$ these two reactions result in a net rate of chemisorption.

First-order chemical reaction

$$R_k = k_k n_s = k_k n_{s0} \Theta \tag{27}$$

R_k rate of kth surface reaction per unit area [$\mathrm{m^{-2}s^{-1}}$]
k_k rate constant [$\mathrm{s^{-1}}$]
n_s surface concentration of reactant [$\mathrm{m^{-2}}$]
Θ fractional surface coverage by reactant

with rate constant following **Arrhenius equation**:

$$k_k = \nu_{0k} \exp(-\frac{E_k}{RT}) \tag{28}$$

ν_{0k} frequency factor or pre-exponential factor
E_k reaction activation energy [kJ/mol]

Assumptions: n_s is constant over time (steady state), chemisorption reaction occurs only in the forward direction (not valid for too high T at which film begins to decompose), adsorption occurs on free sites $\Rightarrow$ **mass balance for the physisorbed precursor**:

$$\Gamma_{\mathrm{i}} \delta (1 - \Theta) = R_r + R_d = (k_r + k_d) n_{s0} \Theta \tag{29}$$

Γ_{i} molecular impingement flux [$\mathrm{m^{-2}s^{-1}}$]
R_r reaction (chemisorption) rate and R_d desorption rate

Sticking Coefficient

Using previous relations we obtain for **surface coverage Θ**

$$\Theta = \frac{\Gamma_{\mathrm{i}}\delta/n_{s0}}{\Gamma_{\mathrm{i}}\delta/n_{s0} + k_r + k_d} \tag{30}$$

and substituing into the chemisorption rate expression (27)

$$R_r = k_r n_{s0}\Theta = \frac{\Gamma_{\mathrm{i}}\delta k_r}{\Gamma_{\mathrm{i}}\delta/n_{s0} + k_r + k_d}. \tag{31}$$

We may now define **sticking coefficient S_{c}** more precisely

$$S_{\mathrm{c}} = R_r/\Gamma_{\mathrm{i}} \tag{32}$$

In case of **small Γ_{i}**, i.e. **small Θ** Eq. (31) simplifies to

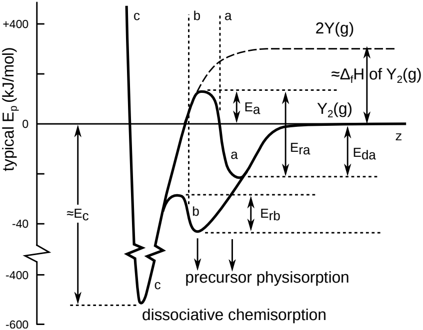
$$R_r = \frac{\Gamma_{\mathrm{i}}\delta}{1 + k_d/k_r} = \Gamma_{\mathrm{i}}\frac{\delta}{1 + \frac{\nu_{0d}}{\nu_{0r}}\exp(\frac{E_r - E_d}{RT_s})} \equiv \Gamma_{\mathrm{i}}\xi. \tag{33}$$

where ξ is **chemisorption reaction probability**.
$S_c \approx \xi$ for $\Theta \ll 1$ but for larger Θ, $S_c < \xi$.
For the special case of film deposition from single vapor having the same composition as the film, $\xi = \alpha_c$ (condensation coefficient).
The assumption of 1st order kinetics is not always valid for a more complicated case of compound-film deposition from multicomponent vapors. For more details refer to book of Donald Smith, chapter 7.3.3.

Activated adsorption

The chemisorption rate R_r governs the rate of film deposition when

- k_r is the same from site to site along the surface
- T_s is not so high that decomposition or re-evaporation of the film occur.



$$R_r = \Gamma_\mathrm{i} \frac{\delta}{1 + \frac{\nu_{0d}}{\nu_{0r}} \exp\left(\frac{E_r - E_d}{RT_s}\right)}$$

If $E_r > E_d$ there is an **activation energy** $E_a = E_{ra} - E_{da}$ for chemisorption (**curve a**). For high E_a the film fail to deposit unless T_s is raised to make exp. term smaller $\Rightarrow R_r \uparrow$ **for** $T \uparrow$
The activated case is very common in CVD.

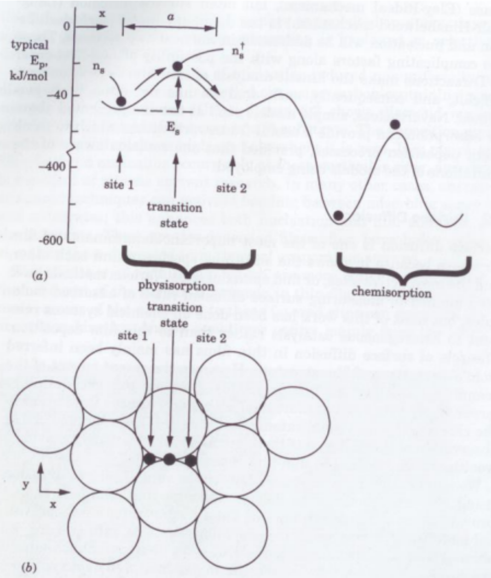
If $E_r < E_d$ (chemisorption is not activated as in **curve b**) $\Rightarrow R_r \downarrow$ **for** $T \uparrow$

Example: Si deposits from SiH_4 at elevated (not room) T_s. If T_s becomes too high, the evaporation flux of the Si $\Gamma_v > R_r$ and deposition stops. The net deposition flux of Si:

$$\Gamma_r = R_r - \Gamma_v \qquad (34)$$

$\Rightarrow T_s$ **window** for deposition.

4.8 Surface Diffusion



Flux of adsorbate Γ_s $[\mathrm{m}^{-1}\mathrm{s}^{-1}]$ across the E_s barrier between 1 and 2 sites in the x direction

Rate of barrier crossing

$$R_s = \frac{\Gamma_s}{a} \qquad (35)$$

a is the distance between the sites.

Considering Maxwell-Boltzmann distribution

$$R_s = \frac{1}{4}\frac{n_s'\bar{v}}{a} = \frac{n_s'}{a}\sqrt{\frac{k_\mathrm{B}T}{2\pi m}} \qquad (36)$$

n_s' - surface concentration of adsorbate residing in the **transition state**.

Relation between n_s' and n_s?
-from statistical physics (next page)

Concentrations in Surface States

Relation between n'_s (concentration in transition states) and n_s (concentration in adsorption states)?

$$\frac{n'_s}{n_s} = \frac{Z'_r Z'_v Z'_t}{Z_r Z_v Z_t}\,\mathrm{e}^{-\left(\frac{E_s}{RT}\right)} \qquad Z = \sum_i g_i\,\mathrm{e}^{-\left(\frac{E_i}{RT}\right)} \tag{37}$$

Z - partition function, g_i degeneracy of the energy level,
r, v, t rotational, vibrational, translation kinetic energies (electronic excitations are neglected at ordinary T),
The Boltzmann factor accounts for the potential energy difference E_s (J/mol) between the adsorption-site state n_s and the transition state n'_s

- rotation of molecules is limited by adsorption $\Rightarrow Z'_r = Z_r = 1$
- Z_{vk} derived from quantum mechanics for harmonic oscillator

$$Z_{vk} = \frac{1}{1 - \exp\left(-\frac{h\nu_k}{k_\mathrm{B} T}\right)} \tag{38}$$

  but vibrational modes are mostly in their ground states at ordinary T
- partition function for translation energy

$$Z'_{tx} = a\frac{\sqrt{2\pi m k_\mathrm{B} T}}{h} \tag{39}$$

$$\Rightarrow \quad n'_s = n_s Z'_{tx} \exp -\left(\frac{E_s}{RT}\right) \tag{40}$$

Rate of barrier crossing

. . . using absolute-reaction-rate theory (predicts the absolute reaction rate of a chemical reaction from the quantum mechanical description of the potential energy changes during the interaction; cannot provide a quantitative estimation of the diffusion rate but gives an insight into the determining factors)

$$R_s = n_s \left(\frac{k_\mathrm{B} T}{h} \right) \exp\left(-\frac{E_s}{RT}\right) = n_s \nu_{0s} \exp\left(-\frac{E_s}{RT}\right) = n_s k_s \tag{41}$$

Arhenius expression for the **rate constant k_s** of "chemical reaction".
The rate constant k_s (s^{-1}) represents the frequency with which an individual adsorbate molecules "hops" to an adjacent site. Thus, the factor $\nu_{0s} = 10^{13} - 10^{16}\ s^{-1}$ is NOT the frequency of any vibrational component ν_k of the adsorbate.

The rate of surface diffusion increases exponentially with ↑ T and ↓ E_s (activation energy for surface diffusion).

- $E_s \ll E_d, E_c$ (desorption activation energy of physisorbed or chemisorbed species, respectively) because the bonds are only partially broken.
- At T of the film deposition approaching the onset of re-evaporation, i. e. when $\exp(-E_c/(RT))$ becomes significant ⇒ high rate of surface diffusion = one of principal ways in which substrate T affects film structure.

E_s/E_c sometimes referred as corrugation ratio, it is lower for metals than for semiconductors due to absence of bond directionality in metals.

Diffusion Length

Relation between **molecular hopping rate** k_s and the distance which an adsorbate molecule travels during the film deposition:

- classic random-walk problem
- The final locations are more widely dispersed from the starting point with increasing time t. For large number of hops N_o, it is Gaussian dispersion $\exp(-\frac{x^2}{2\sigma^2})$ characterized by its standard deviation $\sigma = \Lambda$ - the **diffusion length**

$$\Lambda = r\sqrt{N_o} \approx a\sqrt{N_o} = a\sqrt{k_s t}$$

r is per-hop rms change in the distance from the starting points.

Two regimes need to be considered separately:

- t is time between adsorption and **burial** by the next depositing monolayer
- adsorbate is more likely to **desorb** than to be buried within t

Regime 1 - **burial time**:

$$t = \frac{n_0}{\Gamma_\mathrm{r}} \quad \Rightarrow \quad \Lambda = a\sqrt{\frac{\nu_\mathrm{os} n_0}{\Gamma_\mathrm{r}}} \exp\left(-\frac{E_\mathrm{s}}{2RT}\right)$$

where n_0 is surface density of adsorption sites (m^{-2}), Γ_r deposition flux (m^{-2}s^{-1}) and $k_\mathrm{s} = \nu_\mathrm{os} \exp\left(-\frac{E_\mathrm{s}}{RT}\right)$

Diffusion Length - contin.

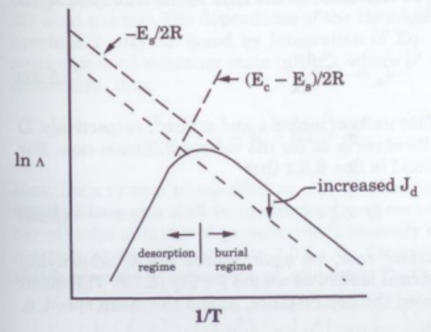
Regime 2 - If T is high enough the film re-evaporation (**desorption**) becomes significant. $\Rightarrow$ **t is adsorption lifetime**. Considering the desoprtion only from chemisorbed state (negligible concentration of precursor state at high T):

$$t = \frac{1}{k_\mathrm{c}} = \frac{1}{\nu_\mathrm{oc}} \exp\left(\frac{E_\mathrm{c}}{RT}\right)$$

where subscript c denotes the chemisorbed state.

Combining both gives

$$\Lambda = a\sqrt{\frac{\nu_\mathrm{os}}{\nu_\mathrm{oc}}} \exp\left(\frac{E_\mathrm{c} - E_\mathrm{s}}{2RT}\right) \tag{42}$$



Diffusion Coefficient

How is the diffusion length Λ (obtained from the examination of motion of individual adsorbed molecules) related to the macroscopic quantity - **diffusion coefficient**?

Transport equation

$$\Gamma_{\mathrm{s}} = -D \frac{\mathrm{d}n_{\mathrm{s}}}{\mathrm{d}x}$$

Γ_{s}, n_{s} have surface units $\mathrm{m}^{-1}\mathrm{s}^{-1}$ and m^{-2}

Using analogy of 3D case $D = \frac{1}{4} v_{\mathrm{av}} \lambda$, in which the mean free path λ is the hop distance a and the mean speed v_{av} is $k_{\mathrm{s}} a$

$$D = \frac{1}{4} k_{\mathrm{s}} a^2 \quad \Rightarrow \quad \Lambda = a\sqrt{k_{\mathrm{s}} t} = 2\sqrt{Dt} \tag{43}$$

Thus, we can express D in the Arrhenius form when using this expression for k_{s}:

$$D = \frac{1}{4} \nu_{\mathrm{os}} a^2 \exp\left(-\frac{E_{\mathrm{s}}}{RT}\right) = D_0 \exp\left(-\frac{E_{\mathrm{s}}}{RT}\right) \tag{44}$$

4.9 Nucleation

Nucleation is a complication that must often **be added to the above described model of chemisorption where we expected that k_r is the same from site to site**.

If nucleation is important, the net deposition flux $\Gamma_r = R_r - \Gamma_v$ is $\Gamma_r > 0$ only for certain active substrate-surface sites, **nucleation sites** or **nuclei of film material** which have spontaneously accumulated.
Various examples:

- Si chemically passivated by H reacts with adsorbates mainly at those few sites that are missing H atom $\Rightarrow R_r \uparrow$ at unpassivated Si surface atoms because of $\downarrow E_r$
- In deposition of compounds from separate vapor sources of each element, adsorbing vapor bonds much more strongly to surface sites occupied by the other element

$$\mathrm{Zn(g)} + \mathrm{Se(a)} \rightarrow \mathrm{ZnSe(c)} \quad \text{and} \quad \mathrm{Se(g)} + \mathrm{Zn(a)} \rightarrow \mathrm{ZnSe(c)}$$

- atoms of low-reactivity metals often bond much less easily to nonmetallic substrates: E_a of chemical bond of Zn, Cd to glass is very high because of high bond strength between substrate elements $\Rightarrow$ Zn, Cd on glass bonds more readily to itself than to the surface $\Rightarrow$ formation of nucleus

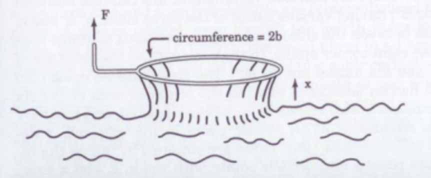
The existence of certain sites which are active in adsorption is common in thin-film processes. Access of precursor to these favored sites can dominate the deposition kinetics. Two types of access

- from vapor phase - **Eley-Rideal mechanism**
- by surface diffusion - **Langmuir-Hinshelwood mechanisms**

Surface tension and energy

Concept of **surface tension** γ has to be introduced to understand nucleation.

The force F required to draw a liquid membrane: $F = 2b\gamma$ (b is circumference, 2 stands for inner and outer surface). Work $F\Delta x$ to create the membrane of area $A = 2b\Delta x$ is stored as surface energy $\Rightarrow$ surface energy per unit area $F\Delta x/A = \gamma$ [N/m]
$\Rightarrow$ **For liquids, surface (free) energy per unit area (J/m^2) is equal to surface tension γ.**



For solids at $T > 0$ K, the surface Gibbs free energy is reduced by entropy factor TS which depends on the degree of surface disorder $\Rightarrow$ surf. energy is minimized by surface diffusion. **Additionally**, in solids, there is an **surface energy term $A\sum_{ij}\sigma_{ij}\mathrm{d}\varepsilon_{ij}$** in which σ_{ij} **is surface stress** and $\mathrm{d}\varepsilon_{ij}$ **surface strain tensor $\sum \mathrm{d}\varepsilon_{ij}\delta_{ij} = \mathrm{d}A/A$.**

Liquids cannot support such strain because the atoms just rearrange to relax it.

Thin-film growth

Nature tends to minimize surface energy γA:

- when wire is lifted far enough, the membrane is in the plane of the ring
- **in solids, surface energy minimizes by surface diffusion $\Rightarrow$ fundamental process to development of structure in thin films**

In thin-film growth, both A and γ are varying:

- A depends on surface topography
- γ depends on many properties of exposed surface (chemical composition, crystallographic orientation, atomic **reconstruction**, atomic-scale roughness etc.). It is **anisotropic** for most crystalline solids.

For deposition onto a foreign substrate, nucleation behaviour is strongly influenced by **surface tension of substrate, γ_{s}**. We also need to consider γ_{i} **of the substrate-film interface** and γ_{f} **of film free surface**.

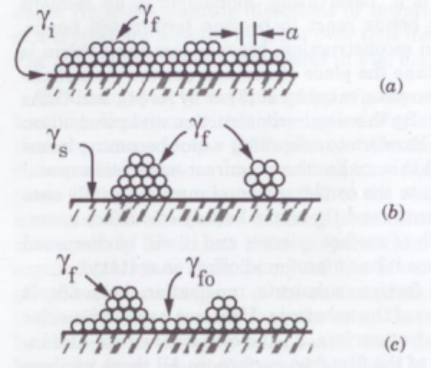
Two cases for growth modes:

- $\Lambda \gg a$, i. e. deposition material can rearrange itself to minimize γ, **nucleation is not kinetically limited and approaches equilibrium**
- $\Lambda < a$ atoms sticks where they land and the **growth behaviour is “quenched”**

Growth Modes for $\Lambda \gg a$ (nucleation is not kinetically limited)

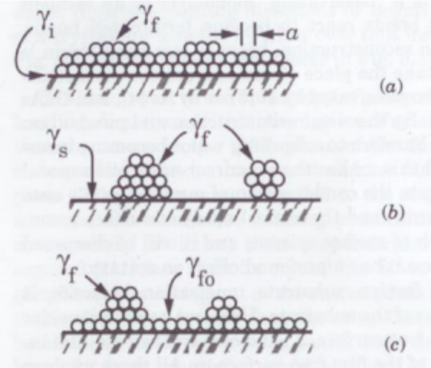
For $\Lambda \gg a$, there are two nucleation situations on the bare substrate

- (a) films wets the substrate because $\gamma_{\mathrm{f}} + \gamma_{\mathrm{i}} < \gamma_{\mathrm{s}} \Rightarrow$ smooth growth, atomic layer by layer (**Frank-van der Merwe growth**). It requires strong enough bonding between film and substrate to reduce γ_{i}
- (b) with insufficient substrate bonding film forms 3D islands (**Volmer-Weber growth mode**). In extreme case of no bonding at all $\gamma_{\mathrm{i}} = \gamma_{\mathrm{f}} + \gamma_{\mathrm{s}}$, the film spreading across the substrate would increase the total surface energy by 2γ_{f}.



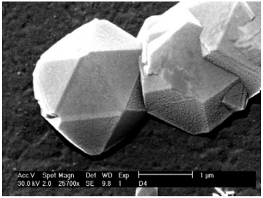
Growth Modes for $\Lambda \gg a$ (contin.)

Third growth mode, **Stranski-Krastanov**, shown in (c) - growth mode changes from layer to island after a monolayer or two due to a change in the energy situation.



2D versus 3D nucleation

3D nucleation is usually undesirable since it leads to rough, nonuniform films (extreme example being the diamond nuclei)



How to manipulated with the growth mode? Film wetting for $\gamma_\mathrm{f} + \gamma_\mathrm{i} < \gamma_\mathrm{s}$.
γ_i decreases with film-substrate bonding (covalent, ionic, metallic). In general, interfacial bonding is stronger between materials having the same type of bonding. Examples:

- chemically-active metal, Cr, will bond to glass by breaking Si-O bond and forming Cr-O
- Au cannot do this, i.e. does not bond well to glass
- Au forms a strong metallic bond to clean Cr

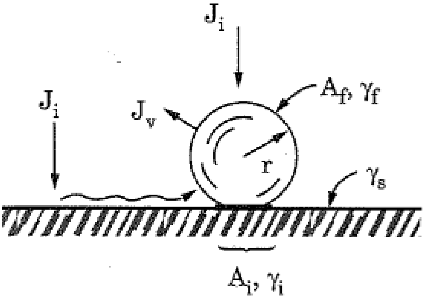
$\Rightarrow$ **Using intermediate "glue" layer (Cr) which bonds well to both, the film and the substrate, γ_i can be reduced and wetting accomplished. Another good bonding material is Ti.**

Alternatively, **energy-enhanced techniques (plasma treatment, ion bombardment, sputtering) can provide the activation energy for bonding between film and substrate, i. e. reduce γ_i.**

3D nucleation - two cases

Two ways in which 3D nuclei can form

- bonding initiates at active surface sites such as atomic steps, crystal deffects, impurities. At these nucleation sites, the E_a is lower than elsewhere.
- even if there are no active nucleation sites, 3D nuclei can still form at random surface locations because of the interfacial bonding which develops by the spontaneous accumulation of mobile atoms plus arriving vapor into “critical” nuclei which are big enough to be stable (classical nucleation problem)



3D nucleation - how to produce smooth & uniform film?

- concentration of critical nuclei n^* has to be ↑
- and their radius $r^* \downarrow$,

i. e. , less coarse nucleation

How to achieve it?

- **Using very high vapor arrival rate** (supersaturation), at least until the nucleation phase is over and the film is continuous. Coarsening will still occur even with one-atom critical nuclei because atoms and nuclei are mobile on the surface ⇒ migration and coalescence
- **Decrease the substrate T** to inhibit surface diffusion ⇒ freezing the nucleation and coalescence. If arriving species do no thave enough energy to desorb or diffuse they remain where they land - quenched growth mentioned earlier. In this case, **the nucleation is kinetically inhibited by the surface-diffusion activation-energy barrier E_s**

4.10 Structure Development

Upon coalescence of the surface nuclei to form a continuous film, the nucleation step of the film deposition is complete and **4th step begins - development of the bulk film structure**. The form of the structure changes dramatically with

- the amount of thermal motion taking place during film growth: **scales with** $T_\mathrm{s}/T_\mathrm{m}$ (substrate T_s over film melting T_m) - known as **homologous** or **reduced** T
- the **amount of additional energy** being delivered to the growth surface

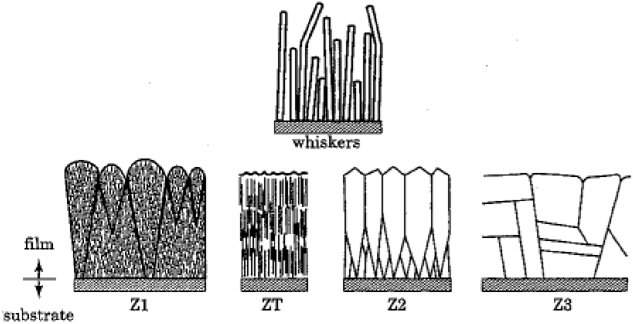


Figure 5.15 Characteristics of the four basic structural zones and of whiskers, in cross section. The ratio of substrate T to film melting T (T_s/T_m) increases in the direction Z1→ZT→Z2→Z3.

4.10 Structure Development

quenched growth - Z1 and ZT ($\Lambda < a$):

- Z1 occurs at $T_\mathrm{s}/T_\mathrm{m}$ **so low** that surface diffusion is negligible, i. e. $\Lambda < a$: **columns** $\approx$ tens of nm in diameter **separated by voids** a few nm across. The columns have **poor crystallinity (many deffects) or are amorphous**.
  In thicker films, an array of cones with wider voids between them become superimposed upon this structure. The cones terminate in domes at the surface, and the size of the domes increases with film thickness.
- ZT also occurs when $\Lambda < a$. It contains defected columns as Z1 but the voids and domes are absent. **ZT is usually associated with energy-enhanced processes.**

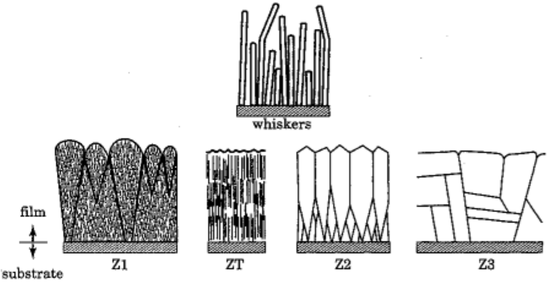


Figure 5.15 Characteristics of the four basic structural zones and of whiskers, in cross section. The ratio of substrate T to film melting T (T_s/T_m) increases in the direction Z1→ZT→Z2→Z3.

4.10 Structure Development

thermally activated rearrangement on or within the film - **Z2 and Z3**:

- **Z2 occurs for $T_\mathrm{s}/T_\mathrm{m} \gtrsim 0.3$, diffusion becomes significant:** columns having tight grain boundaries and a characteristic diameter which increases with $T_\mathrm{s}/T_\mathrm{m}$. Crystalline columns are less defected than in Z1 and ZT, and are often facetted at the surface. The Z2 structure can also accur in amorphous films. The column boundaries are planes of reduced bonding rather than planes of crystallographic discontinuity.
- **Z3 occurs at certain instances at $T_\mathrm{s}/T_\mathrm{m} > 0.5$:** considerable bulk annealing of the film is taking place during deposition, more isotropic crystallite shapes.

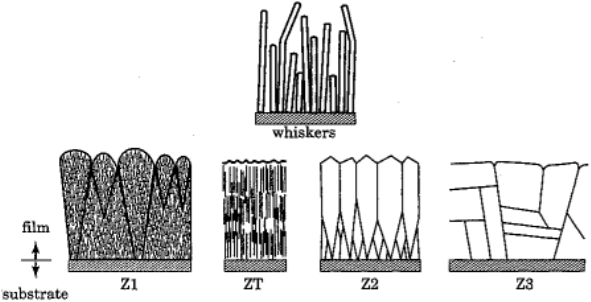


Figure 5.15 Characteristics of the four basic structural zones and of whiskers, in cross section. The ratio of substrate T to film melting T (T_s/T_m) increases in the direction Z1→ZT→Z2→Z3.

Quenched growth

Simple model of statistical roughnening caused by statistical fluctuation in the vapor arrival flux: each atom is constrained to stick on the site it lands on (even if it is on top of a pillar)

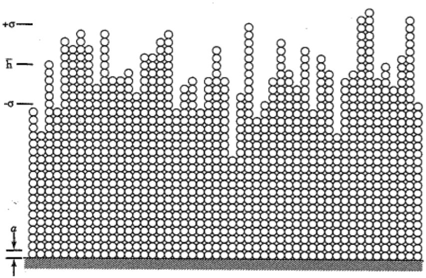


Figure 5.16 Statistical roughening in random ballistic deposition of a 25-atom-thick film. (Pascal solution courtesy of Jared Smith-Mickelson.)

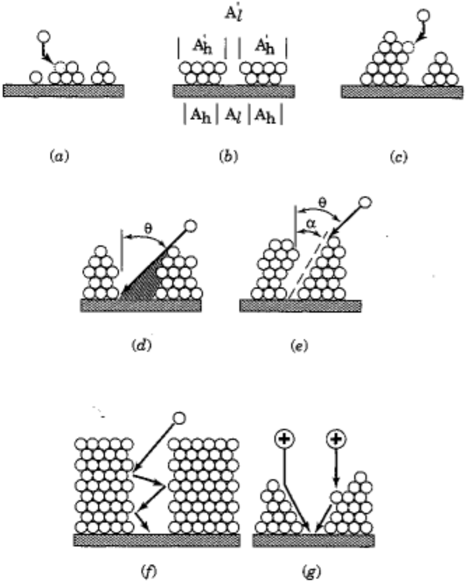
For large enough $\bar{N}$ (average number of atoms per depositing site)
the variation in heights is described by Gaussian distribution with standard deviation

$$\sigma = a\sqrt{\bar{N}} = \sqrt{a\bar{h}}$$

where $\bar{h} = a\bar{N}$ is average film thickness

Note: analogy to dispersion in lateral direction arising from surface diffusion because both are random processes

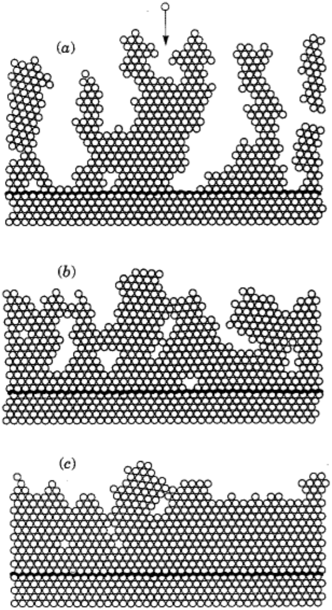
Quenched growth



Atomistic processes in quenched-growth structure development (more realistic model):

- (a) ballistic aggregation (arriving atoms cannot perch on top of each other but rather settle sideways)
- (b) effect of atoms finite size (shadowing low areas)
- (c) sideways attraction (development of columns)
- (d) oblique shadowing (self-shadowing, incidence over range of θ occurs for fluid-flow regime $Kn \ll 1$)
- (e) tilt effect
- (f) low sticking coefficient
- (g) void-filling by energetic particle due to enhanced mobility (left) and forward sputtering (right)

Quenched growth - void filling by energetic particles



2D MD simulation of the deposition of energetic atoms impinging perpendicularly onto a substrate held at 0 K.

The horizontal line is substrate interface.

$E_t/E_c =$ incident energy / adatom potential-well depth

- (a) $E_t/E_c = 0.02$
- (b) $E_t/E_c = 0.5$
- (c) $E_t/E_c = 1.5$

Thermally activated growth

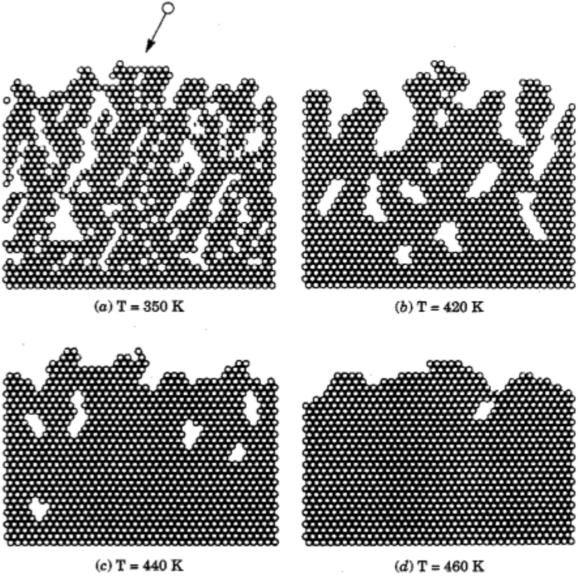

(a) T = 350 K (b) T = 420 K (c) T = 440 K (d) T = 460 K

Figure 5.20 Two-dimensional computer simulation of the effect of substrate T on void filling by surface diffusion. (Source: Reprinted from Ref. 22 by permission.)