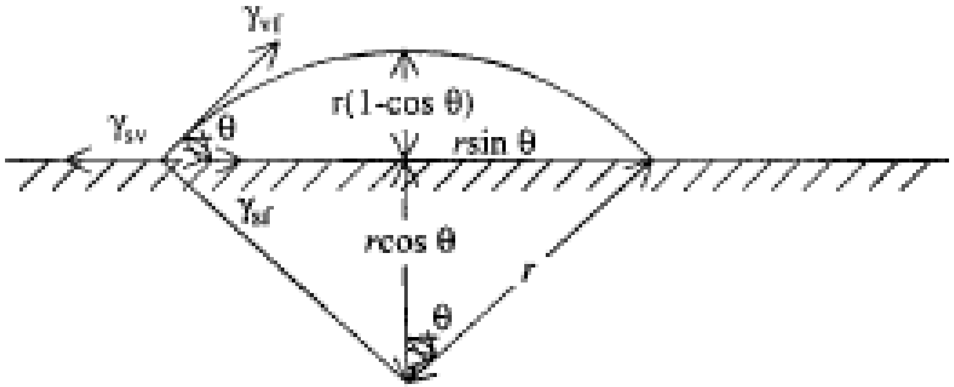
Heterogenous Nucleation

(Ref: Guozhong Cao; Nanostructures & Nanomaterial: Synthesis, Properties & Applications)

- When new phase forms on a surface of another material, process is called HETEROGENEOUS NUCLEATION.
- Let us consider the process on a planar solid substrate.
- Assuming growth species in Vapor Phase and it impinge on substrate surface.
- Growth species diffuse and aggregate to form a nucleus with a cap shape as shown in figure.
- Decrease in Gibbs free energy and increase in surface/interface energy will be observed similar to homogeneous nucleation process.



Heterogeneous Nucleation process with related surface energy in equilibrium

- Total change of chemical energy, ΔG, associated with the formation of nucleus is given by:

$$\Delta G = a_3 r^3 \Delta\mu_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv};$$

where r is mean dimension of nucleus, $\Delta\mu_v$ is the change of Gibbs Free Energy per unit volume,

γ_{vf}, γ_{fs}, γ_{sv} are the surface/interface energy of vapor-nucleus, nucleus-substrate, and substrate-vapor interfaces, respectively.

Respective geometric constants are given by:

$a_1 = 2\pi(1 - \cos\theta)$

$a_2 = \pi \sin^2\theta$

$a_3 = 3\pi(2 - 3\cos\theta + \cos^2\theta)$

where r is mean θ is the contact angle and depends on the surface properties of interface involved and defined by Young's equation:

$\gamma_{sv} = \gamma_{fs} + \gamma_{vf} \cos\theta$

- In analogy to homogeneous nucleation, formation of new phase results in reduction of Gibbs free energy with in total surface energy.
- Nucleus is stable, when its size is larger than critical size, r*:

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

and the critical energy barrier, ΔG*, is given by:

$$\Delta G^* = \frac{4(a_1\gamma_{vf}+a_2\gamma_{fs}-a_2\gamma_{sv})^3}{27a_3^2\Delta G_v}$$

Substituting all geometric constants, we get:

$$r^* = \frac{2\pi\gamma_{vf}}{\Delta G_v}\left\{\frac{sin^2\theta.cos\theta+2\ cos\theta-2}{2-3\ cos\theta+cos^3\theta}\right\}$$

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

- Comparing the values with critical energy equation ΔG* for homogeneous nucleation, which is $\frac{16\pi\gamma}{(3\Delta G_v)^2}$. We can see that the first term in the above equation represents the values of critical energy barrier for homogeneous nucleation, where as the second term is a wetting factor.
- When the contact angle is 180°, new phase does not wet on substrate at all, the wetting factors equal to 1 and the critical energy barrier becomes the same as that of homogeneous nucleation.
- When the contact angle is less than 180°, energy barrier for heterogeneous nucleation is always smaller than that of homogeneous nucleation, which explains the fact that heterogeneous nucleation is easier than homogeneous nucleation in most cases.
- When the contact angle is 0°, wetting factor will be zero and there is no energy barrier for the formation of new phase.
- Example of such cases is that the deposit is the same material as the substrate.

- For the synthesis of nanoparticles and quantum dots on substrate, $\theta > 0$ is required and accordingly Young's equation becomes

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$$

- Such Heterogeneous nucleation is generally referred as Island Growth (Volmer-Weber) in thin films community.
- Other two nucleation modes are layer growth (Frank-Van der Merwe) and island-layer growth (Stranski-Krastanov).
- Formation of nanoparticles through heterogeneous nucleation is different from the synthesis by vapor phase reaction.
- For homogeneous nucleation in vapor phase, particles are first formed in vapor phase and then deposited onto substrate surfaces.
- For heterogeneous nucleation, growth species impinge onto and form nuclei on substrate surfaces.

Synthesis of 1-D Nanostructures: Nanowires and Nanorods

- One-dimensional nanostructures is also called as whiskers, fibers/fibrils, nanowires and nanorods.
- In many cases, nanotubules and nanocables are also considered as 1-D structures.
- 1-D structures with diameters ranging from several nanometers to several hundred microns is referred as whiskers and fibers.
- Nanowires and nanorods diameter will not exceed few hundred nanometers.
- Nanowires have high aspect ratio (ratio of width to height) than nanorods.
- Synthesis and formation of 1-D nanostructured materials can be grouped into four categories:

  (1) Spontaneous growth (Bottom-Up Approach)

  (2) Template based synthesis (Bottom-Up Approach)

  (3) Electrospinning (Bottom-Up Approach)

  (4) Lithography (Top-Down Approach)

Spontaneous growth can be classified in three categories:

(a) Evaporation/Dissolution – Condensation

(b) Vapor/Solution – Liquid – Solid (VLS or SLS) growth

(c) Stress-induced recrystallization

- Spontaneous growth is a process driven by reduction of Gibbs free energy or chemical potential.
- Reduction of Gibbs free energy is realized by phase transformation/chemical reaction/release of stress.
- For the formation of nanowires/nanorods, anisotropic growth (crystal grows along a certain orientation faster than other directions) is required.
- Defects and impurities on the growth surfaces can play a significant role in determining the morphology of the final products.

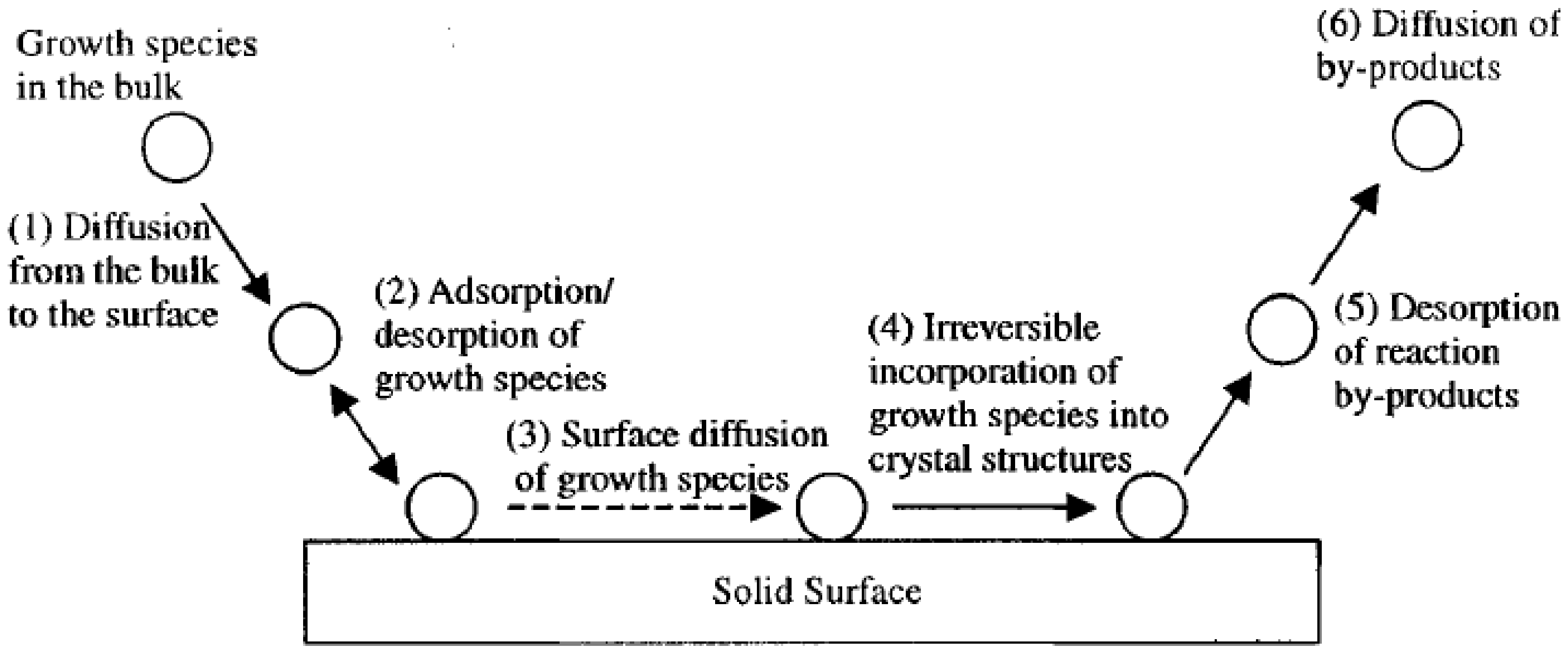
Evaporation (Dissolution) – Condensation growth

- Evaporation-Condensation process is also referred as Vapour Solid (VS) process.
- Driving force for the synthesis of nanorods and nanowires by spontaneous growth is a decrease in Gibbs free energy, which arises from either recrystallization or a decrease in supersaturation.
- Nanowires & nanorods grown by evaporation-condensation methods are single crystal with fewer imperfections.
- Formation of nanowires, nanorods or nanotubes through evaporation (or dissolution) – condensation is due to anisotropic growth.
- Several mechanisms are known to result in anisotropic growth. For example:
  1. Different facets in a crystal have different growth rate. E.g. in silicon with diamond structure, growth rate of {111} facets is smaller than {110}.
  2. Presence of imperfections in specific crystal directions such as screw dislocation.
  3. Preferential accumulation of or poisoning by impurities on specific facets.

Review of the fundamentals of crystal growth

- Crystal growth can be considered as heterogeneous reaction.

- Typical crystal growth proceeds following the sequences as sketched below:



Schematic illustrating six steps in crystal growth, which can be generally considered as a heterogeneous reaction, and a typical crystal growth proceeds following the sequences

1. Diffusion of growth species from the bulk (vapor or liquid phase) to the growing surface, which, in general, is considered to proceed rapid enough and, thus, not at a rate limiting process.
2. Adsorption and desorption of growth species onto and from the growing surface. The process can be rate limiting, if the supersaturation or concentration of growth species is low.
3. Surface diffusion of adsorbed growth species. During surface diffusion, an adsorbed species may either be incorporated into a growth site, which contributes to crystal growth, or escape from the surface.
4. Surface growth by irreversibly incorporating the adsorbed growth species into the crystal structure. When a sufficient supersaturation or a high concentration of growth species is present, this step will be the rate-limiting process and determines the growth rate.
5. If by-product chemicals were generated on the surface during the growth, by products would desorb from the growth surface, so that growth species can adsorb onto the surface and the process can continue.
6. By-product chemicals diffuse away from the surface so as to vacate the growth sites for continuous growth.

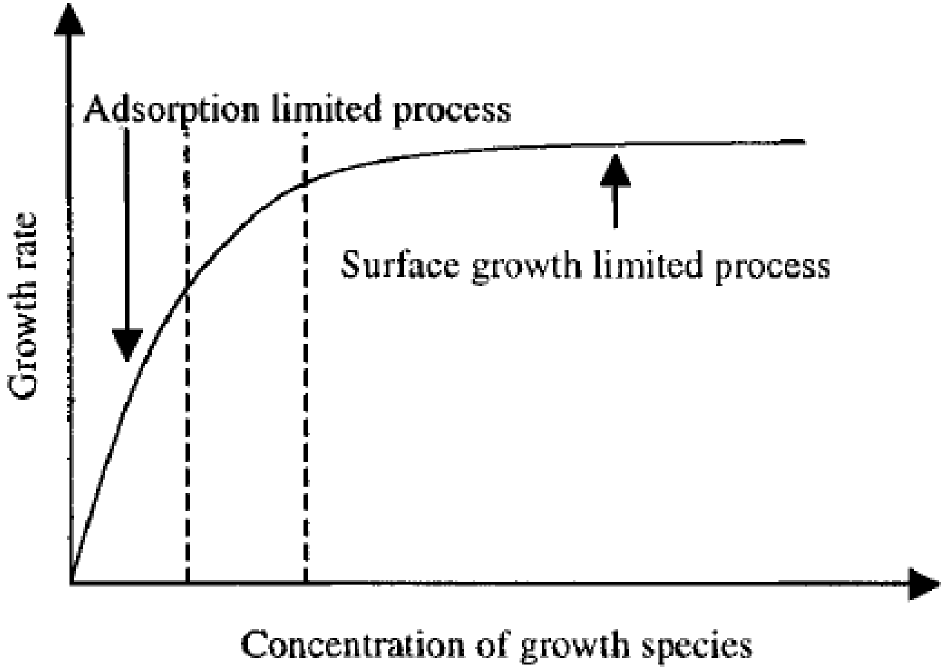
- For most crystal growth, rate limiting step is either adsorption-desorption of growth species on the growth surface (step 2) or surface growth (step 4).
- When step 2 is rate limiting, growth rate is determined by condensation rate, J (atoms/cm^2 sec), which is dependent on the number of growth species adsorbed onto the growth surface, which is directly proportional to vapor pressure or concentration, P, of the growth species in the vapor as given by:

$$J = \frac{\propto \sigma P_0}{\sqrt{2\pi m k T}}$$

where α is accommodation coefficient, $\sigma = \frac{P - P_0}{P_0}$ is the supersaturation of growth species in the vapor in which P_0 is the equilibrium vapor pressure of the crystal at temperature T, m is the atomic weight of the growth species and k is Boltzmann constant.

- Accommodation coefficient, α, is the fraction of impinging growth species that becomes accommodated on the growing surface, and is a surface specific property.
- Surface with a high accommodation coefficient will have a high growth rate as compared with low α surfaces.
- Significant difference in accommodation coefficients in different facets would result in anisotropic growth.
- When the concentration of growth species is very low, adsorption is more likely a rate limiting step.
- For a given system, growth rate increases linearly with increase in concentration of growth species.
- Further increase in concentration of growth species would result in a change from an adsorption limited to surface growth limited process.
- When surface growth becomes a limiting step, growth rate becomes independent of concentration of growth species as shown in schematic diagram on next slide.
- High concentration or vapor pressure of growth species in the vapor phase would increase the probability of defect formation, such as impurity inclusion and stack faults.

- Further, a high concentration may result in a secondary nucleation on the growth surface or even homogeneous nucleation, which would effectively terminate the epitaxial or single crystal growth.
- An impinging growth species onto the growth surface can be described in terms of residence time and/or diffusion distance before escaping back to the vapor phase.



Relation between growth rate and reactant concentration. At low concentration, growth is diffusion limited and thus increases linearly with increasing reactant concentration. At high concentration, surface reaction is the limited step and thus the growth rate becomes independent of reactant concentration.

- The residence time, τ_s, for a growth species on the surface is described by;

$$\tau_s = \frac{1}{\nu} \exp\left(\frac{E_{des}}{kT}\right)$$

where ν is the vibrational frequency of the adatom, i.e. adsorbed growth species, on the surface (typically 10^{12} sec^{-1}), E_{des} is the desorption energy required for growth species escaping back to the vapor.

- While residing on the growth surface, a growth species will diffuse along the surface with the surface diffusion coefficient, D_s, given by:

$$D_s = \frac{1}{2} a_0 \nu\, exp\left(\frac{-E_s}{kT}\right)$$

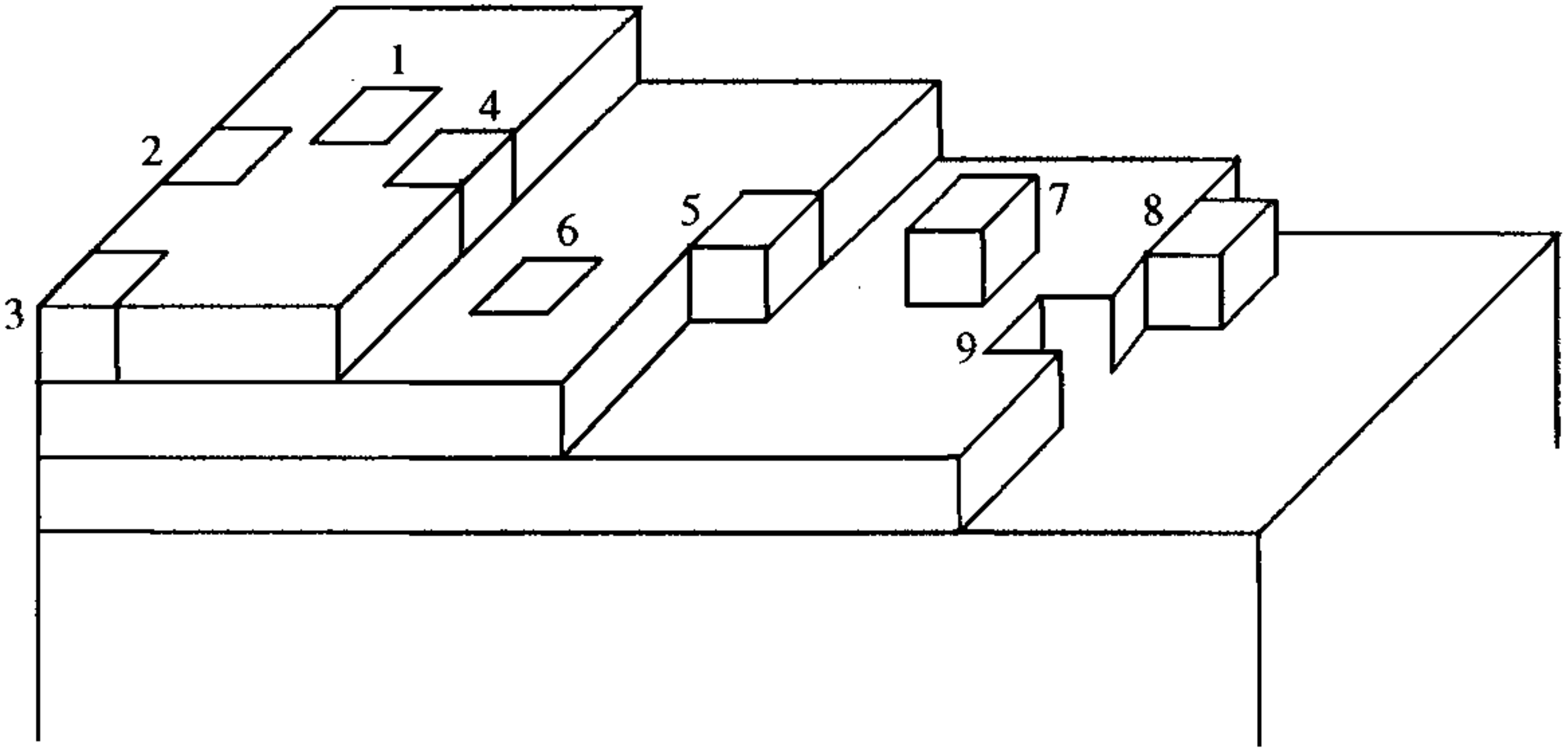
where E_s is the activation energy for surface diffusion and a_0 is the size of growth species.

- Mean diffusion distance, X, for a growth species from the site of incidence can be expressed as:

$$X = \sqrt{2}\, D_S \tau_S = a_0\, exp\left(\frac{E_{des} - E_s}{kT}\right)$$

- It is clear that in a crystal surface, if the mean diffusion distance is far longer than the distance between two growth sites such as kinks or ledges, all adsorbed growth species will be incorporated into the crystal structure and the accommodation coefficient would be unity.
- If the mean diffusion distance is far shorter than the distance between growth sites, all adatoms will escape back to the vapor and the accommodation coefficient will be zero.
- The accommodation coefficient is dependent on desorption energy, activation energy of surface diffusion and the density of growth sites.
- When step 2 proceeds sufficiently rapid, surface growth (step 4) becomes a rate limiting process.
- Different facets in a given crystal have different atomic density and atoms on different facets have different number of unsatisfied bonds (also referred as broken or dangling bonds), leading to different surface energy.
- Such a difference in surface energy or the number of broken chemical bonds leads to different growth mechanisms and varied growth rates.

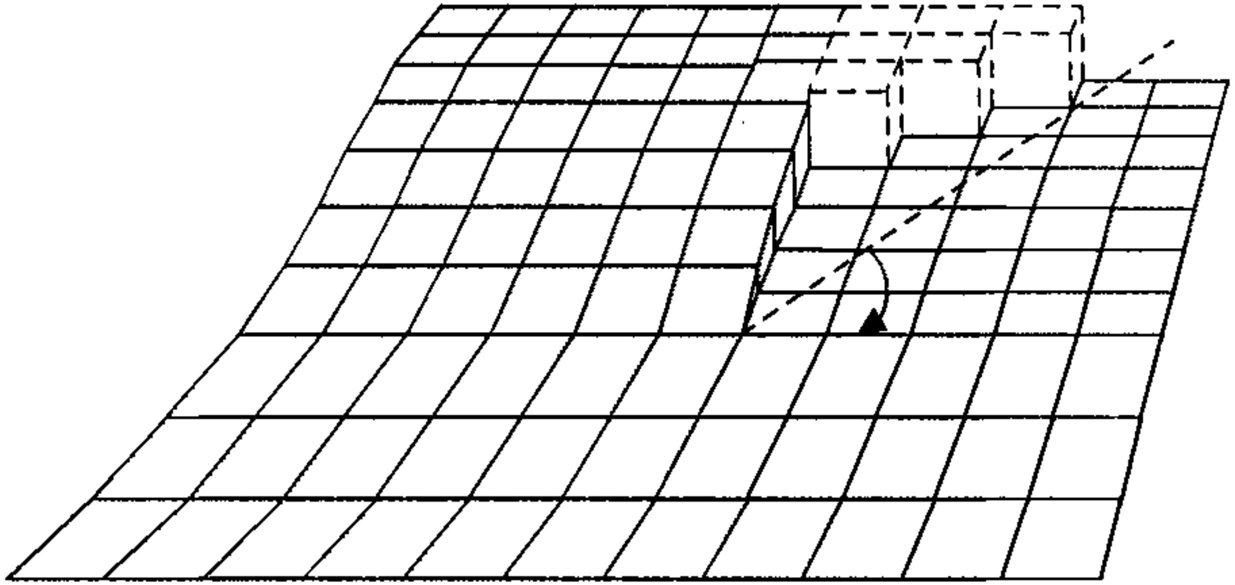
- According to Periodic Bond Chain (PBC) theory developed by Hartman and Perdok, all crystal facets can be categorized into three groups based on the number of broken periodic bond chains on a given facet: FLAT SURFACE, STEPPED SURFACE and KINKED SURFACE.
- The number of broken periodic bond chains can be understood as the number of broken bonds per atom on a given facet.
- For flat surface, classic theory was developed by KOSSEL, STRASKI and VOLMER (KSV) Theory.
- They recognized that crystal surface, on atomic scale, is not smooth, flat or continuous.
- This discontinuities are responsible for crystal growth.
- To illustrate step growth mechanism, let us consider {100} surface of simple cubic crystal with each atom as a cube with coordination number six (six chemical bonds), as shown in next slide.



Schematic illustrating the step growth mechanism, considering {100} surface of a simple cubic crystal as an example and each atom as a cube with coordination number of six (six chemical bonds) in bulk crystal.

- When atom adsorbs onto the surface, it diffuses randomly on the surface.
- When it diffuses to an energetically favourable site, it will be irreversibly incorporated into the crystal structure, resulting in the growth of the surface.
- However, it may escape from the surface back to the vapor.

- On a flat surface, an adsorbed atom may find different sites with different energy levels.
- An atom adsorbed on a terrace would form one chemical bond between the atom and surface; such an atom is called an adatom, which is in a thermodynamically unfavourable state.
- If an adatom diffuses to ledge site, it would form two chemical bonds and become stable.
- If an atom were incorporated to a ledge-kink site, three chemical bonds would be formed.
- An atom incorporated to kink site would form four chemical bonds.
- Ledge, ledge-kink and kink sites are all considered as growth sites.
- Incorporation of atoms into these sites is irreversible and results in growth of the surface.
- The growth of a flat surface is due to advancement of the steps (ledges).
- For a given crystal facets and a given growth condition, growth rate will be dependent on the step density.
- A misorientation would result in an increased density of steps and consequently lead to a high growth rate.
- Increased step density would favour irreversible incorporation of adatoms by reducing surface diffusion distance between the impinging site and growth site, before adatoms escape back to vapor phase.
- Limitation of this growth mechanism is the regeneration of growth sites, when all available steps are consumed.
- BURTON, CABRERA and FRANK (BCF) proposed screw dislocation serves as a continuous source to generate growth sites so that the stepped growth would continue (as shown in figure shown on next slide).



Crystal growth proceeds in a spiral growth, known as BCF theory, in which screw dislocation serves as a continuous source to generate growth sites so that the stepped growth would continue.

- The crystal growth proceeds in a spiral growth, and this growth mechanism is now known as BCF theory.
- Presence of screw dislocation will not only ensure the continuing advancement of the growth surface, but also enhance the growth rate.
- The growth rate of given crystal facet under a given experimental condition would increase with an increased density of screw dislocations parallel to growth direction.
- It is also known that different facets can have different ability to accommodate dislocations.
- Presence of dislocations on certain facet can result in anisotropic growth, leading to formation of nanowires or nanorods.

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