

## Lecture 30: Kinetics of Epitaxial Growth: Surface Diffusion and

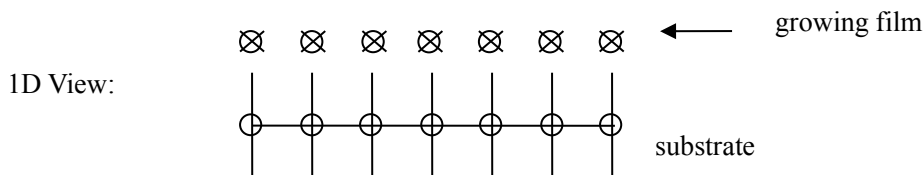
### Nucleation

#### Today's topics

- Understanding the basics of epitaxial techniques used for surface growth of crystalline structures (films, or layers).
- The kinetics of epitaxial growth is determined by the surface diffusion and nucleation.
- Understanding the three thermodynamic modes of epitaxial growth: competition between the three interface energies.

#### Basics of Epitaxial Growth:

- **Epitaxy** refers to the method of depositing a mono-crystalline film on a mono-crystalline substrate. The deposited film is denoted as epitaxial film or epitaxial layer. The term epitaxy comes from the Greek roots --- epi, meaning "above", and taxis, meaning "in ordered manner". So, "epitaxial" can be translated "to arrange upon".

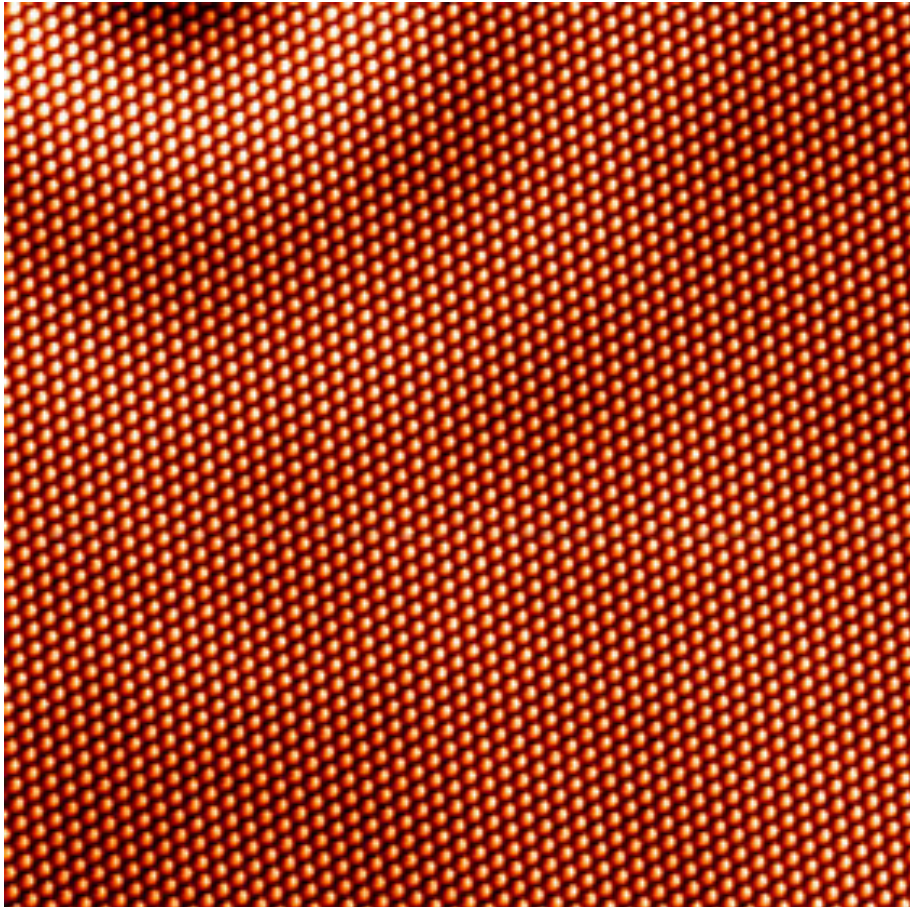


- Epitaxial films may be grown from gaseous or liquid precursors. Because the substrate acts as a seed crystal, the deposited film takes on a lattice structure and orientation identical to those of the substrate. This is different from other thin-film deposition methods which deposit polycrystalline or amorphous films, even on single-crystal substrates.
- Epitaxial films can be classified into two categories: **homoepitaxy**, for which the film is deposited on a substrate of the same composition; and **heteroepitaxy**, for which the film is deposited on a substrate of different.
- **Homoepitaxy** is a kind of epitaxy performed with only one material. In homoepitaxy, a crystalline film is grown on a substrate or film of the same material. This technology is used to grow a film which is more pure than the substrate and to fabricate layers having different doping levels. In academic literature, homoepitaxy is often abbreviated to "**homoepi**".
- **Heteroepitaxy** is a kind of epitaxy performed with materials that are different from each other. In heteroepitaxy, a crystalline film grows on a crystalline substrate or film of a different material. This technology is often used to grow crystalline films of materials for which single crystals cannot

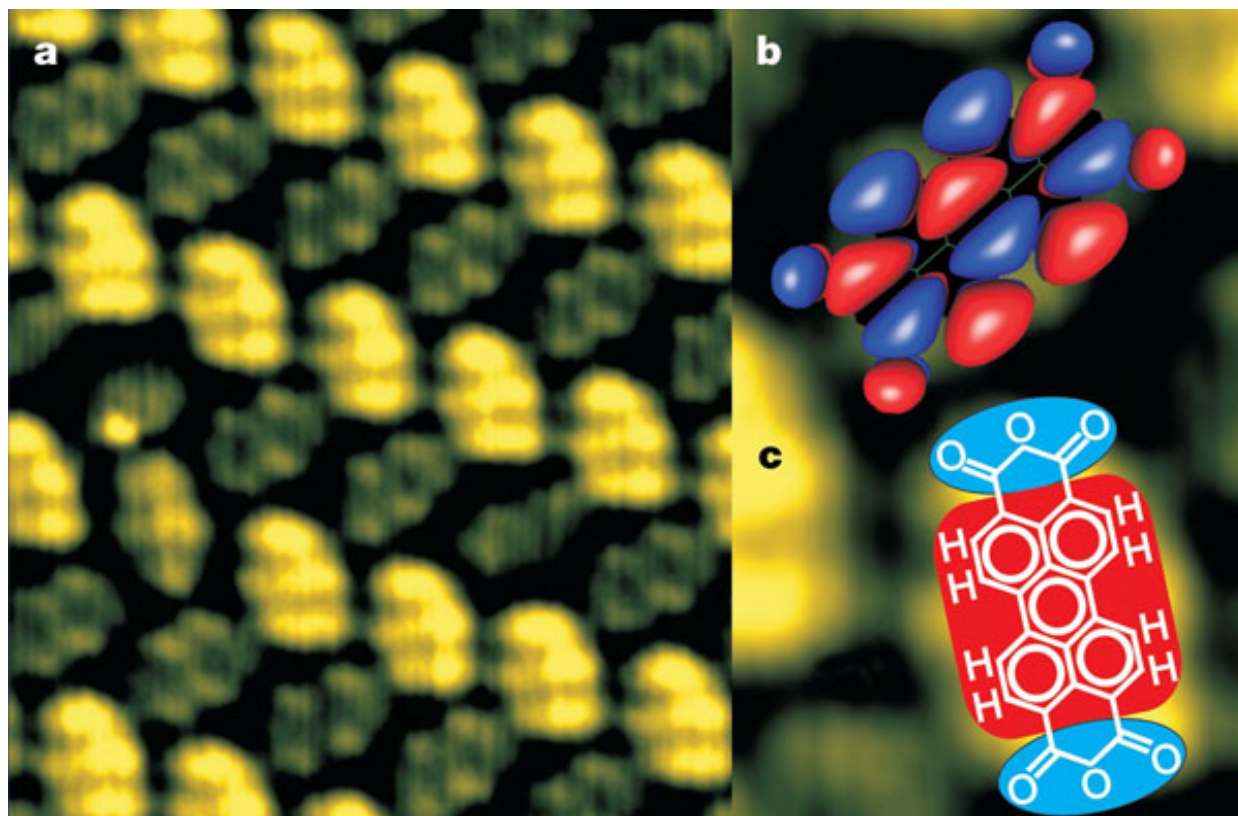
otherwise be obtained and to fabricate *integrated crystalline layers* of different materials. Examples include gallium nitride (GaN) on sapphire or aluminum gallium indium phosphide (AlGaInP) on gallium arsenide (GaAs).

#### **Applications of Epitaxial Growth:**

- Epitaxy is used in **nanotechnology** and in **semiconductor** fabrication. Indeed, epitaxy is the only affordable method of high quality crystal growth for many semiconductor materials, including technologically important materials as silicon-germanium, gallium nitride, gallium arsenide, indium phosphide and graphene.
- Epitaxy is also used to grow layers of pre-doped silicon on the polished sides of silicon wafers, before they are processed into semiconductor devices. This is typical of power devices, such as those used in pacemakers, vending machine controllers, automobile computers, etc.
- Recently, epitaxy has been used to deposit organic molecules onto crystalline substrate to form organized layer → **molecular electronics!**

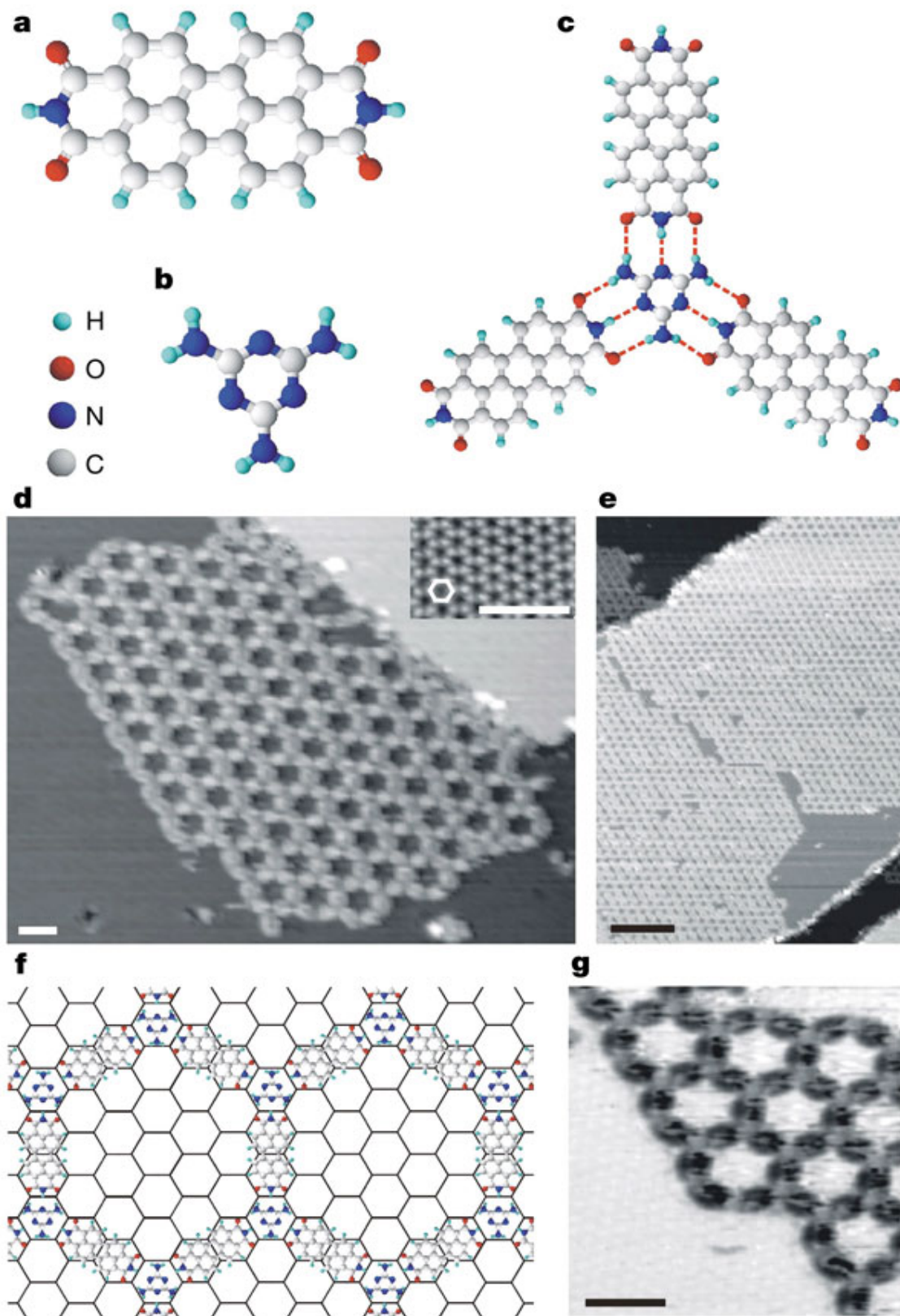


Ag(111) surface by STM, 13X13 nm, T:5K



Understanding and tuning the epitaxy of large aromatic adsorbates by molecular design,  
Nature, 2003, Oct. 9, 425, 602-605





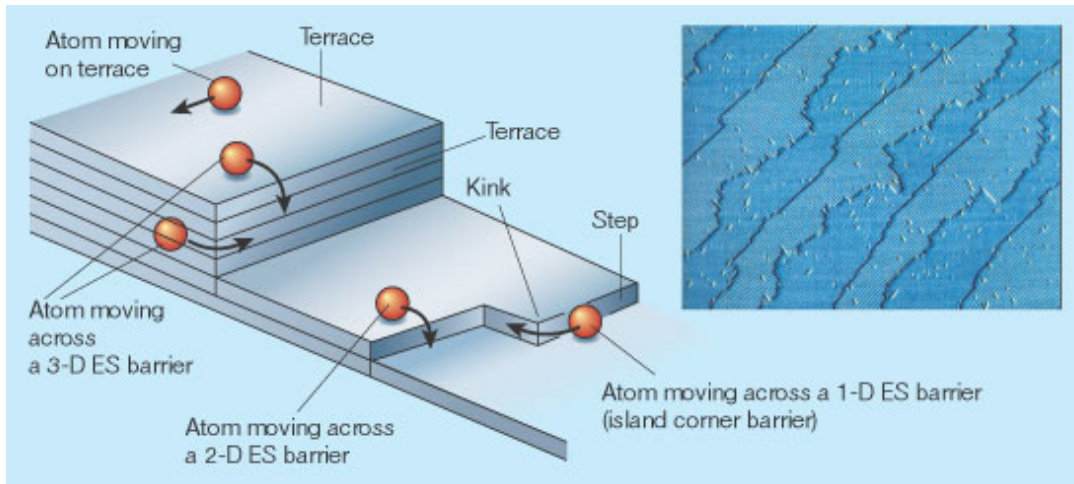
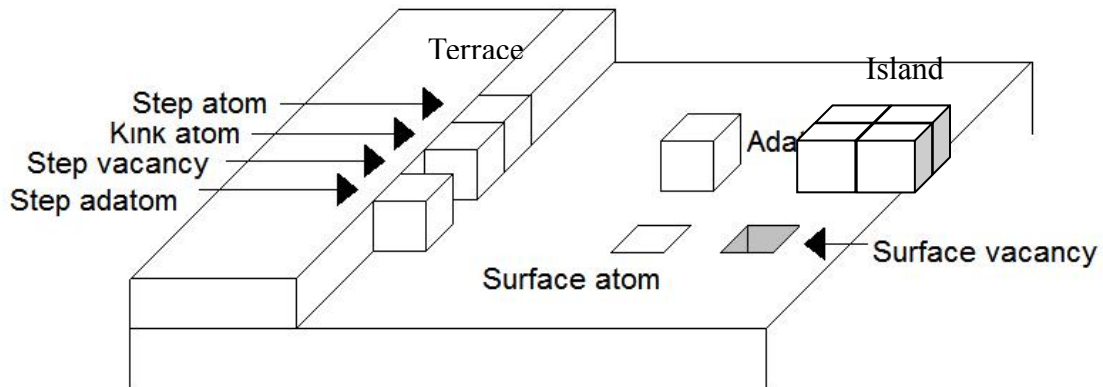
Controlling molecular deposition and layer structure with supramolecular surface assemblies  
 Nature, 2003, August 28, Vol424, 1029-1031

**Description of crystalline surface: Terrace Step Kink (TSK) model**

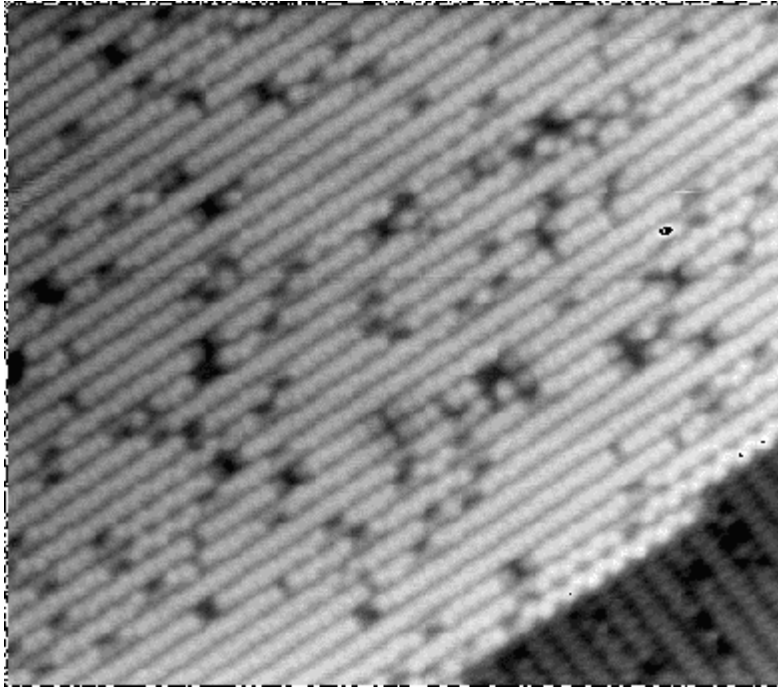
TSK model, also referred to as **Terrace Ledge Kink (TLK)** model, describes the thermodynamics of crystal surface formation and transformation, as well as the energetics of surface defect formation. The TSK model can be applied successfully to surface science topics such as crystal growth (including epitaxial growth), surface diffusion, roughening, and vaporization, because it considers the two major points about the surface:

1. The **energy of an atom's position** on a crystal surface is determined by its bonding to neighboring atoms;
2. Phase **growth or transition** simply involve the counting of broken and formed bonds.

The TSK model was originally proposed by **Kossel and Stranski**.



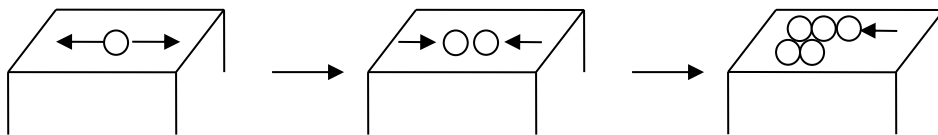
(note: ES barrier refers to Ehrlich-Schwoebel (ES) step-edge barrier)



An STM image of the Si(001) surface. There is a **step** in the bottom right corner.

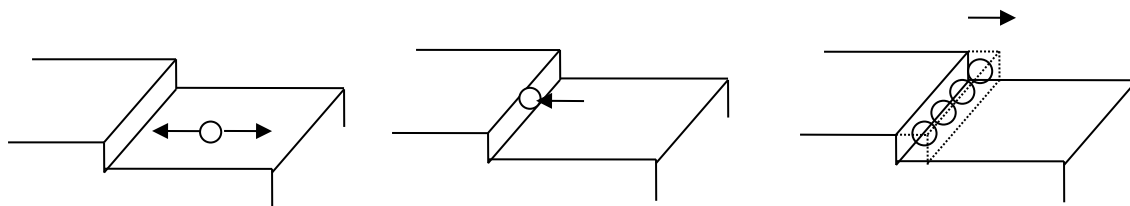
**Modes of epitaxial growth: regarding kinetics**

1. Layer-by-layer: diffusion  $\rightarrow$  nucleation  $\rightarrow$  growth.



Condition: low temperature, high flux, low step density

2. Step-flow: diffusion  $\rightarrow$  sticking to step  $\rightarrow$  step flow



Condition: high temperature, low flux, high step density.

**Modes of epitaxial growth:**

**regarding thermodynamics, i.e., competition between surface/interface energies**

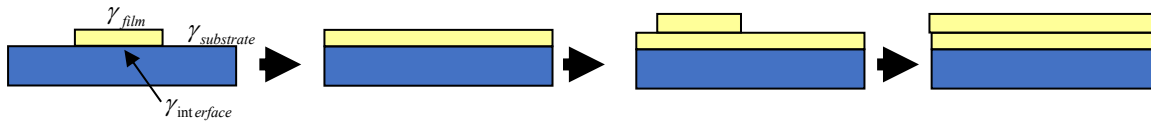
1. **Frank-van der Merwe mode:** Layer-by-layer growth, wetting

$$\gamma_{substrate} \geq \gamma_{film} + \gamma_{interface}$$

$\gamma_{substrate}$  : surface energy of substrate

$\gamma_{film}$  : surface energy of film

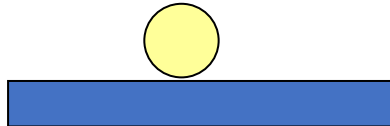
$\gamma_{interface}$  : interface energy between film and substrate



Growing layer reduces surface energy, leading to complete wetting of the surface, and thus smooth, layer-by-layer growth.

2. **Vollmer-Weber mode:** island growth, non-wetting

$$\gamma_{substrate} < \gamma_{film} + \gamma_{interface}$$

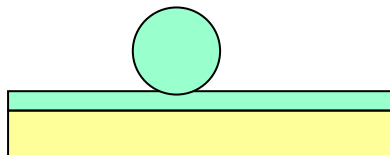


Growing layer increases the interface energy and its own surface energy, leading to layer “balls up” on the substrate.

3. **Stranski-Krastanov (SK) mode:** Layer-by-layer followed by island growth

Initially,  $\gamma_{substrate} \geq \gamma_{film} + \gamma_{interface}$

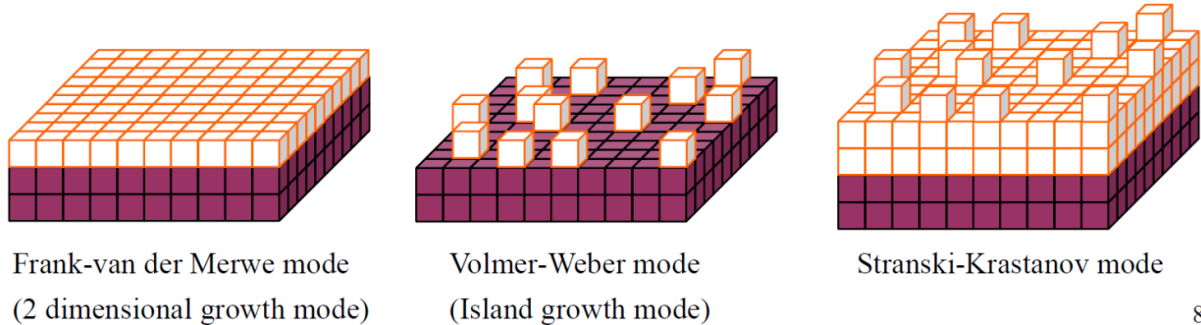
Finally,  $\gamma_{substrate} < \gamma_{film} + \gamma_{interface}$  (due to strain effect)



Typically, first layer wets surface but subsequent layers do not. Change in balance of forces is often due to strain

in the growing layer, typically due to a mismatch in lattice constants between the substrate and the deposited layer.

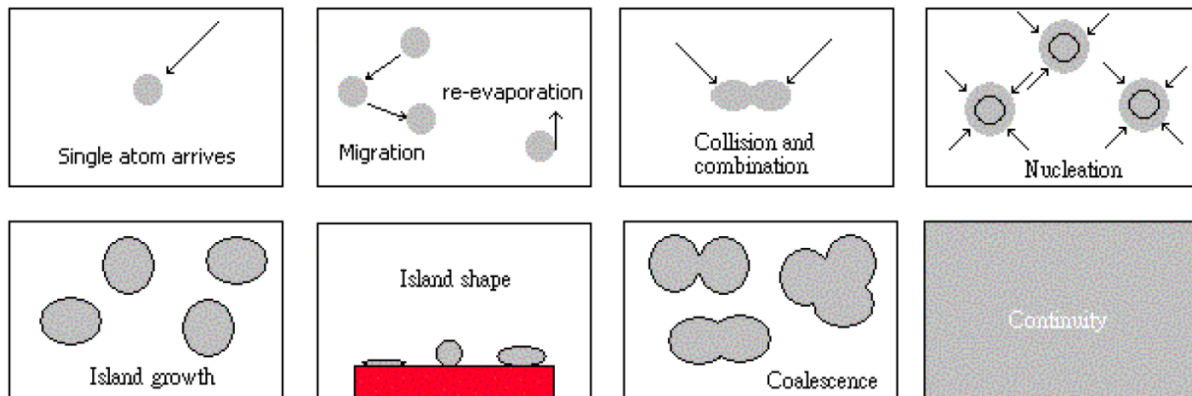
**Comparison between the three thermodynamic growth modes:**



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**Surface Diffusion and Island Density:**

# Thin Film Growth Process



The deposition of adatoms onto a surface form a 2D gas of atoms. The super-saturation leads to condensation through nucleation to growth of 2D or 3D islands.

An arriving adatom makes a random walk on terrace, it has two fates:

- either meets another adatom forming a stable nucleus (**nucleation**) → forming new islands;
- or meets an existing island and stick to it (**growth**).

The competition between nucleation and growth is determined by adatom diffusion coefficient.

For example, a large diffusion coefficient means a *high probability for an adatom to find an existing island* before another adatom is deposited in its vicinity to provide chance for nucleation, leading to an overall **lower island density**. Therefore, there is a relation between surface diffusion and island density.



**Now let's analyze the relationship between surface diffusion and island density:**

*In practice: the larger the diffusion coefficient,  $D$ , the lower the island density,  $N$ . --- we will see if this is consistent with the theory by the end of this note.*

In a 2D random walk, the diffusion coefficient is

$$D = \Gamma \cdot a^2$$

Where “ $\Gamma$ ” is the number of jumps in unit time (second) and “ $a$ ” is the jumping step size, i.e., lattice spacing (see Lecture 3-4).

The lifetime of an adatom is controlled by two collision rates,  $W_{AA}$  (adatom-adatom collision) and  $W_{AI}$  (adatom-island collision).

The “death rate” of adatom, i.e., # of adatoms die in unit time (sec) is

$$n / \tau_A = 2W_{AA} + W_{AI}$$

Where  $\tau_A$  is the lifetime, and  $n$  is the number density of adatoms --- # of adatoms per unit area.

Now, Let  $R$  be the deposition rate --- # of adatoms deposited on unit area in unit time, then

$$n = R\tau_A$$

The number of sites visited by an adatom within unit time (i.e., after  $\Gamma$  jumps) is  $\Gamma$ , so during its lifetime, an adatom visits  $\Gamma \tau_A = D\tau_A / a^2$  sites.

For a unit area, the total number (#) of atomic sites is  $1/a^2$ , and the probability of an atomic site being occupied by an existing adatom is  $n/(1/a^2) = na^2$ , where  $n$  is the number density of adatoms --- # of adatoms per unit area. Similarly, the probability of an atomic site being occupied by an existing island is  $N/(1/a^2) = Na^2$ , where  $N$  is the number density of islands --- # of islands per unit area. Note: here we ignore the difference in size between the adatoms and island, i.e., one island covers one atomic site, and the probability of coverage is proportional to the number density of islands.

Hence, the *probability* of an arriving adatom to collide with an existing atom is  $\frac{D\tau_A}{a^2} \times na^2 = nD\tau_A$

Similarly, the *probability* of an arriving adatom to collide with an existing island is  $\frac{D\tau_A}{a^2} \times Na^2 = ND\tau_A$

Multiplying the above two terms by  $n / \tau_A$  gives the collision rate, i.e., **# of collisions in unit time**:

$$W_{AA} = n^2 D; \quad W_{AI} = nND$$

At the very beginning of deposition,  $N \sim 0$ ,  $\rightarrow W_{AI} = nND \rightarrow 0$ , so, “death rate” of adatom, i.e., # of

adatoms die in unit time,  $n / \tau_A = 2W_{AA}$  --- determined only by the atom-atom collision.

As mentioned above, for an arriving adatom with large enough diffusion, it can always find an existing island before colliding with another coming adatom to form new nucleus, that is, the *probability* of an arriving adatom to collide with an existing island is  $\rightarrow 100\%$  (1.0):

$$ND\tau_A = 1$$

Then,  $\tau_A = 1 / ND$

Now we have,

$$n = R\tau_A = R / ND$$

The nucleation rate, i.e., the rate of increase of the number density of islands, can be given as

$$\frac{dN}{dt} = W_{AA} = n^2 D$$

Substituting n with  $n = R / ND$

Then,  $\frac{dN}{dt} = n^2 D = \frac{R^2}{N^2} \cdot \frac{1}{D}$

Now,  $N^2 dN = \frac{R^2}{D} \cdot dt$

Integration leads to

$$N^3 = (3 \cdot R^2 / D)t = \frac{3R\theta}{D}$$

where  $\theta = Rt$ , is the total deposition (coverage) up to time t.

apparently,

$$N \sim \left(\frac{R}{D}\right)^{1/3}$$

Experimentally, we can measure N, and from there we can determine D.

**Apparently: the larger the diffusion coefficient, D, the lower the island density, N.**