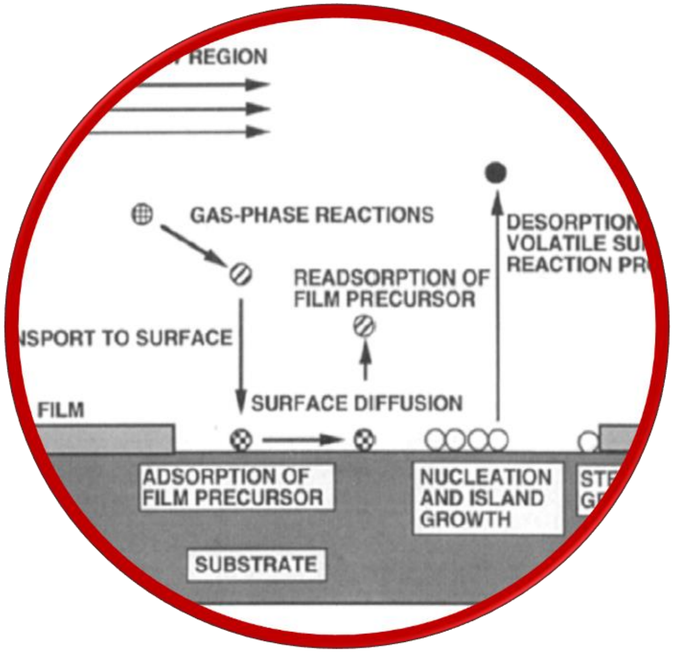
Substrate surfaces and thin film nucleation



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introduction

Sequence of events: **nucleation, growth, coalescence**

a **uniform distribution of small but highly mobile clusters** or islands

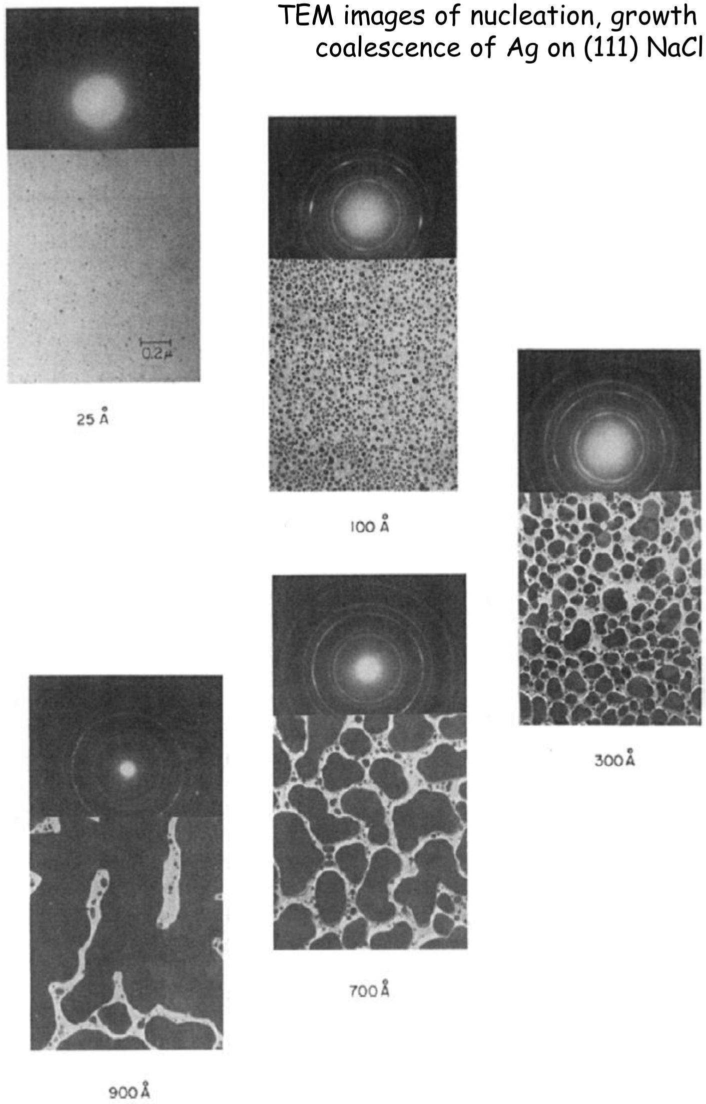
merging of the islands by a coalescence decreasing the island density resulting in local denuding of the substrate where further nucleation can then occur

Continued coalescence & development of a **connected network** with unfilled channels in between

the channels fill in and shrink leaving isolated voids behind

Finally, even the voids fill in completely and the film is said to be continuous.

This **sequence of events occurs during the early stages of deposition**, typically accounting for the first few hundred angstroms of film thickness.



TEM images of nucleation, growth and coalescence of Ag on (111) NaCl.

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introduction

Many observations of subsequent film formation have pointed to **three basic growth modes**:

(1) island (or Volmer-Weber),

(2) layer (or Frank-Van der Merwe), and

(3) Stranski-Krastanov

Island growth happens when atoms or molecules in the deposit are **more strongly bound to each other** than to the substrate. Metal and semiconductor films deposited on oxide substrates initially form such islands.

The opposite characteristics are displayed during **layer growth**. Here the extension of the smallest stable nucleus occurs overwhelmingly in two dimensions, resulting in the formation of planar sheets. In this growth mode the **atoms are more strongly bound to the substrate** than to each other.

The layer plus island or **Stranski-Krastanov** (S-K) growth mechanism is an intermediate combination of the preceding two modes. In this case after forming one or more monolayers, subsequent layer growth becomes unfavorable and islands form.

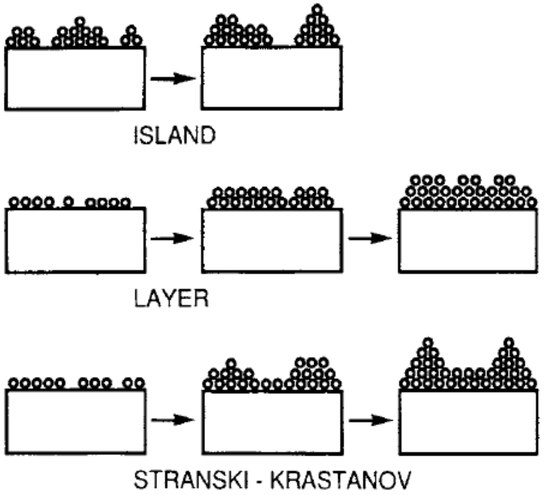

Figure 7-2 Basic modes of thin-film growth.

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Surface structures

If the surface structure is the **predictable extension of the underlying lattice**, we have the case shown in a.

However, **a loss of periodicity in the vertical direction** alters surface electronic properties and leaves energetic broken bonds. It is then more likely that the structure shown in b will prevail.

The absence of bonding forces to underlying atoms results in new equilibrium positions which deviate from those in the bulk lattice. A **disturbed surface layer known as the "selvedge"** may then be imagined. Within this layer the **atoms relax in such a way as to preserve the symmetry of the bulk lattice parallel to the surface**, but not normal to it.

A more extreme structural disturbance is depicted in c, where **surface atoms rearrange into a structure with a symmetry that differs** from that of the bulk solid. This phenomenon is known as **reconstruction** and can alter many surface structure-sensitive properties, e.g., chemical, electrical, optical, and sorption behavior.

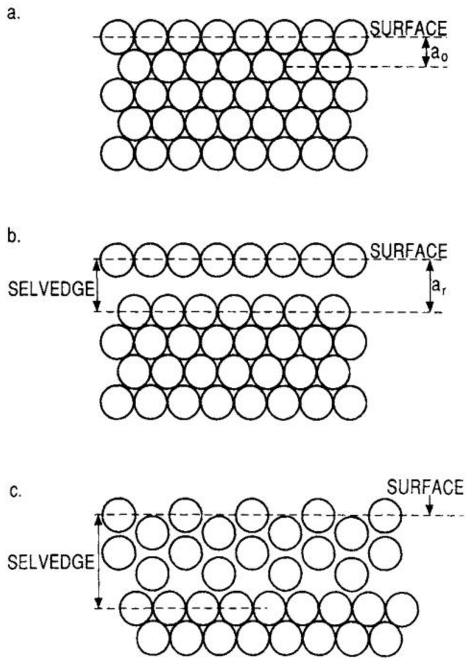

Figure 7-5 Schematic cross-sectional views of close-packed atomic positions at a solid surface. (a) Bulk exposed plane. (b) Atomic relaxation outward. (c) Reconstruction of outer layers.

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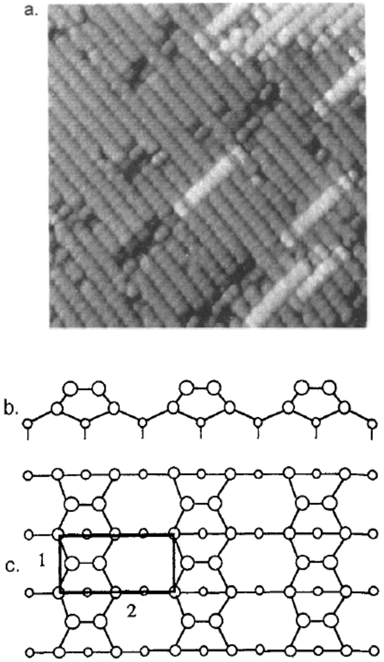
Reconstructed (001) silicon surfaces

On a clean (001) Si surface, atoms are surprisingly **not arranged according to the much reproduced bulk diamond-cubic lattice** structure where the nearest-neighbor atom separation is 0.385 nm.

Instead, the isotropic facecentered square array of Si atoms assumes **an anisotropic reconstructed structure of lower symmetry** possessing two characteristic directions. These lie in the surface plane either along or perpendicular to dimer (paired atom) rows in orthogonal <110> orientations. The parallel dimer rows aligned at 135° with respect to the page horizontal, are easily visible in the STM image.

Schematically shown in both side and top views of Figs. b and c is the **(2 x 1) reconstructed surface** structure on (001) Si. In these figures the position of silicon atoms, differentiated by circle size, is shown at three successive levels.



STM

Side view

Top view

Figure 7-8 (a) Scanning tunneling microscope image of parallel dimer rows. (From Ref. 35.) (b) Schematic side view of the reconstructed (001) Si surface having a (2 × 1) structure. (c) Top view of reconstructed (2 × 1) Si surface. The intensified unit cell measures 0.385 nm × 0.770 nm. (From Ref. 8.) (Reprinted with the permission of Max G. Lagally.)

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Adsorption reactions on solid surfaces

Let expose a pristine substrate surfaces to gas particles.

The first thing is **surface adsorption**--the process in which impinging atoms and molecules enter and interact within the transition region between gas phase & surface

Two kinds of adsorption processes, namely physical (**physisorption**) and chemical (**chemisorption**),
can be distinguished depending on the strength of the atomic interactions.

If the particle (molecule) is **stretched or bent but retains its identity**, and **van der Waals forces** bond it to the surface, then we speak of **physisorption**.

Chemisorption is involved when the particle **changes its identity through ionic or covalent bonding** with substrate atoms.

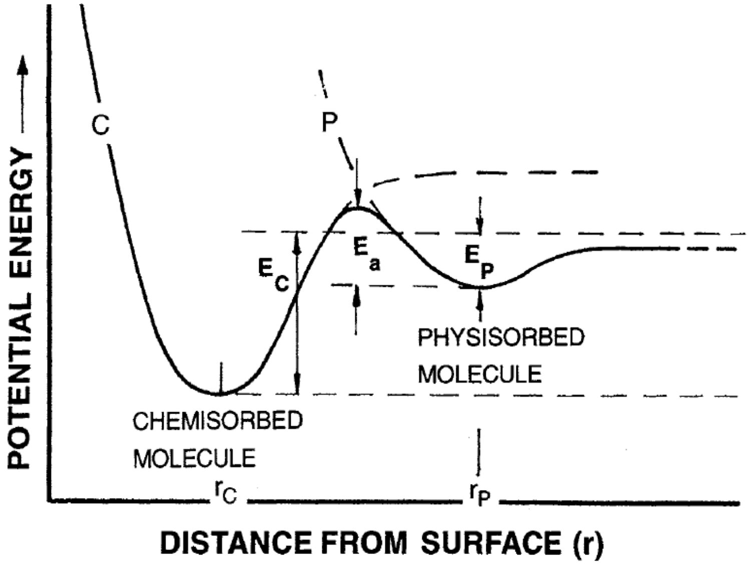

Figure 7-10 Model of physisorption and chemisorption processes in terms of the interaction potential between adsorbate and surface vs distance.

The two sorptions can be quantitatively distinguished on the basis of **adsorption heats or energies, Ep and Ec**, for physisorption and chemisorption, respectively.

Typically **Ep ~ 0.25 eV** while **Ec ~ 1-10 eV**.

It is evident that physisorbed particles achieve equilibrium further from the surface.

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Thermodynamic aspects – surface energies

Capillarity or droplet theory of homogeneous nucleation: **a solid nucleates** from a prior unstable liquid or vapor phase **by respectively establishing** a **solid-liquid (s-l)** or **solid-vapor (s-v) interface**.

Associated with these interfaces or surfaces are corresponding interfacial energies. **Atoms at free surfaces are more energetic** than atoms within the underlying bulk because they make fewer bonds with surrounding atoms and are thus less constrained.

The **difference in interatomic energy of atoms at these two locations is the origin of surface energy**. Alternatively, there is a thermodynamic driving force to reduce the number of necessarily cut, dangling bonds at the surface through rebonding between atoms. We may then equivalently view the surface energy γ (J/m^2) in terms of the energy reduction per unit area.

Metals have higher surface energies than oxides, alkali halides, sulfides, and organic substances. For virtually all elements in the liquid and solid states the surface energies roughly span the range **0.2 to 3 J/m^2 with 1 J/m^2 being typical**. The higher values are associated with the transition metals while the lower values are indicative of alkali and divalent metals, metalloids, and inert gases.

For **organic and aqueous solutions** γ is often **less than 100 mJ/m^2**. Furthermore, the surface energy drops slightly with temperature T; typically, $dT/dT \sim -0.05\ mJ/m^2$

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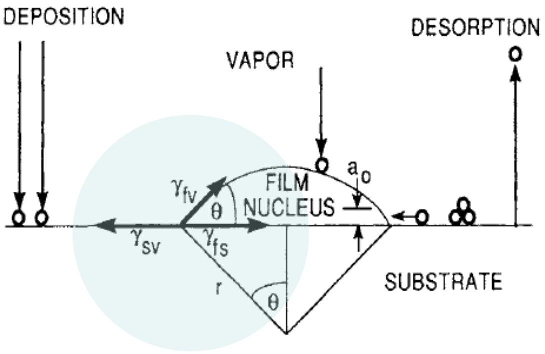
Capillary theory of nucleation

film forming atoms or molecules in the vapor phase impinge on the substrate creating nuclei of mean dimension r. The free-energy change accompanying the formation of such an aggregate is given by

$$\Delta G = a_3 r^3 \Delta G_V + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}.$$



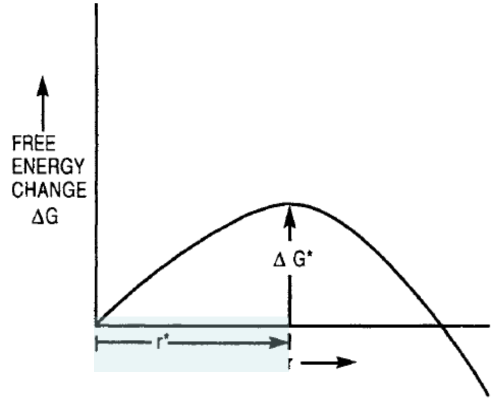
The **mechanical equilibrium** among the horizontal components of the interfacial tensions or forces surrounding the nucleus yields **Young's equation**,

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos\theta \qquad \text{or} \qquad \cos\theta = (\gamma_{sv} - \gamma_{fs})/\gamma_{fv}.$$

Importantly, the contact or wetting angle Θ, which figures prominently in the formulas for r* and ΔG^* developed later, depends solely on the surface properties of the involved materials.

Thermodynamic equilibrium is achieved when $d\Delta G/dr = 0$, which occurs at a **critical nucleus size r = r*** given by

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



For the spherical cap-shaped solid nucleus the curved surface area (a_1r^2), the projected circular area on the substrate (a_2r^2), and the volume ($a_3 r^3$) are involved, and from simple geometry:

$$a_1 = 2\pi(1 - \cos\theta),\ a_2 = \pi \sin^2\theta, \text{ and } a_3 = \tfrac{\pi}{3}(2 - 3\cos\theta + \cos^3\theta).$$

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Capillary theory of nucleation

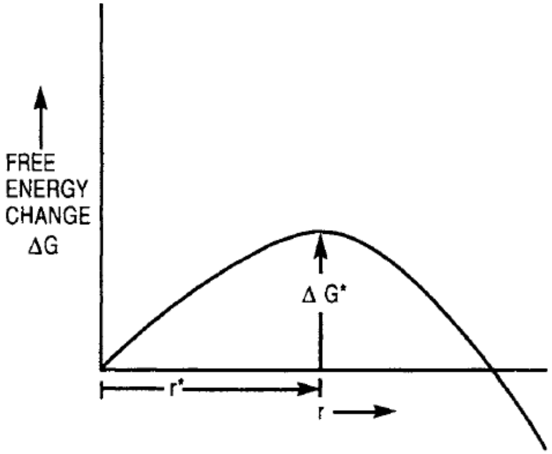
ΔG* represents an energy barrier to the nucleation process.

If a solid-like spherical cluster of atoms momentarily forms by some thermodynamic fluctuation, but with **radius less than r*, the cluster is unstable** and will shrink by losing atoms.

Clusters larger than r* have surmounted the nucleation energy barrier and **are stable**. They tend to grow larger while lowering the overall system energy.

We can now calculate ΔG* as ΔG(r*)

$$\Delta G^* = \frac{16\pi(\gamma_{fv})^3}{3(\Delta G_V)^2}\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\}.$$



The first is the value for ΔG* derived for **homogeneous nucleation**. It is **modified by the bracketed term, a wetting factor dependent on Θ** which has the value of zero for $\Theta = 0°$ and unity for $\Theta = 180°$. When the film wets the substrate, there is no barrier to nucleation. At the other extreme of dewetting, ΔG* is maximum and equal to that for homogeneous nucleation.

This formalism can be expanded to include that the film nucleus is elastically strained or that surface impurities change the surface energy.

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Capillary theory of nucleation

The most important thing to remember about ΔG^* is its strong influence on the density (N*) of stable nuclei that can be expected to survive. Based on our previous experience of associating the probable concentration of an entity with its characteristic energy through a Boltzmann factor:

$$N^* = n_s \exp - \Delta G^*/k_B T,$$

it is appropriate to take ΔG^* as $\Delta G(r^*)$

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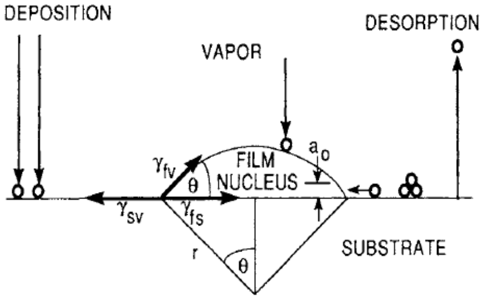
film growth modes

Young's equation provides a mean to understand growth modes. **For island growth**:

$$\gamma_{sv} < \gamma_{fs} + \gamma_{fv}.$$

If γ_{fs} is neglected, this relation suggests that **island growth** occurs when the **surface tension of the film exceeds that of the substrate**. This is why deposited metals tend to cluster or ball up on ceramic or semiconductor substrates.



In the case of layer growth **the deposit "wets" the substrate** and $\Theta = 0°$ and therefore

$$\gamma_{sv} \geqslant \gamma_{fs} + \gamma_{fv}.$$

A special case of this condition is ideal **homo- or "auto-epitaxy."** Because the interface between film and substrate essentially vanishes, γ_{fs} **= 0**. High quality epitaxial films require the avoidance of any disruption to layer growth.

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Strained layers

The **strain energy (G_s) density is relaxed in a 3D island.** In a 2D layer we have

$$G_S = \tfrac{1}{2} Y \varepsilon^2$$

With Y is the elastic modulus of a layer and ε is its strain. For the strain we use the **misfit f** as

$$f = [a_0(s) - a_0(f)]/a_0(f),$$

Where a_0 is the lattice parameter.
Rather than view the breakdown of epitaxy due to dislocation generation, let us consider the **critical film thickness** beyond which a planar film surface roughens due to the growth of islands.

The net free energy change for the **nucleation of a hemispherical island** (not spherical cap) on top of a growing, strained epitaxial layer of thickness h is given by

$$\Delta G = \frac{2\pi r^3}{3} \Delta G_V + \pi r^2 \gamma + \Delta G_S.$$

In the process the island is assumed to be incoherent (or relaxed). The term ΔG_s is interpreted as the difference in epilayer strain energy per unit area after the island nucleates relative to that in the epilayer prior to island nucleation. Therefore, $\Delta G_S = \frac{1}{2}(\varepsilon^2 - f^2) Y h A$, where ε is the mean misfit in the strained film and A =πr^2) is the area affected by strain. We use now $d\Delta G/dr = 0$.

$$r^* = -\frac{[\gamma - \frac{1}{2}(\varepsilon^2 - f^2) Y h]}{\Delta G_V}$$

And in the limit that r*=0

$$h^* = \frac{2\gamma}{(\varepsilon^2 - f^2) Y}.$$

the critical film thickness (h*) for the onset of the **rough island morphology (e.g., S-K growth)**

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the critical film thickness (h*) for the onset of the **rough island morphology (e.g., S-K growth)**

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Growth modes

This relation implies that h* varies approximately as $1/f^2$.

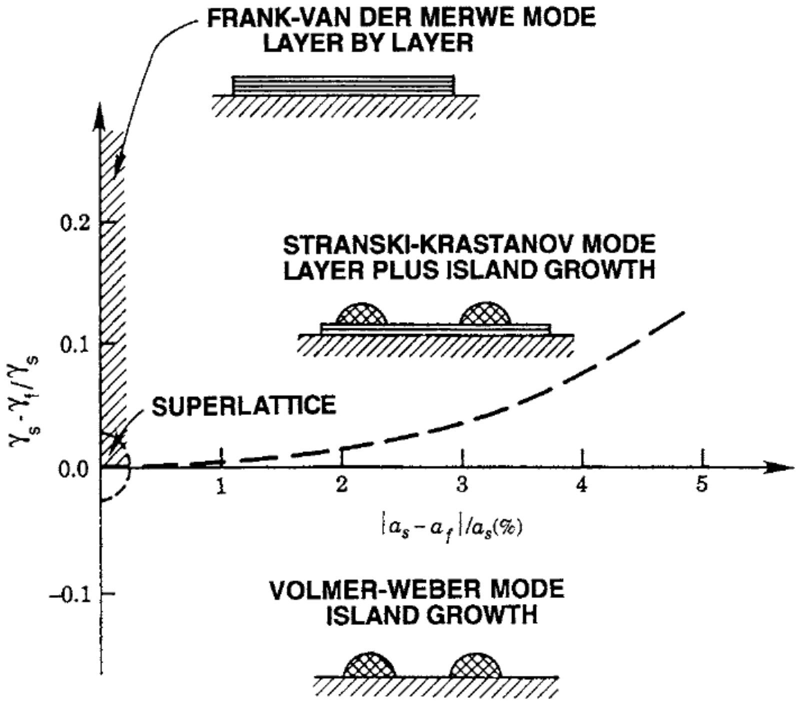
Example: For InGaAs on GaAs, it has been calculated that $h^*(\mathrm{cm}) \times f^2 = 1.8 \times 10^{-10}$ holds.

If we assume as an example an In concentration leading to a misfit of 1% , then the film would grow to a thickness of

$h^*=1.8\times10^{-6}\mathrm{cm}=10\mathrm{nm}$

in a 2D growth mode and beyond 10nm in an island growth mode, which is called the Stranski-Krastanov growth mode.

The figure distinguishes the regimes of influence for the three film growth modes in terms of surface energy ratio.
If $\gamma_f > \gamma_s$ = **is**land growth dominates. But its range of dominance expands when there is additional misfit present. In between island and layer film morphologies, and competing with them, is therefore the S-K growth mode.



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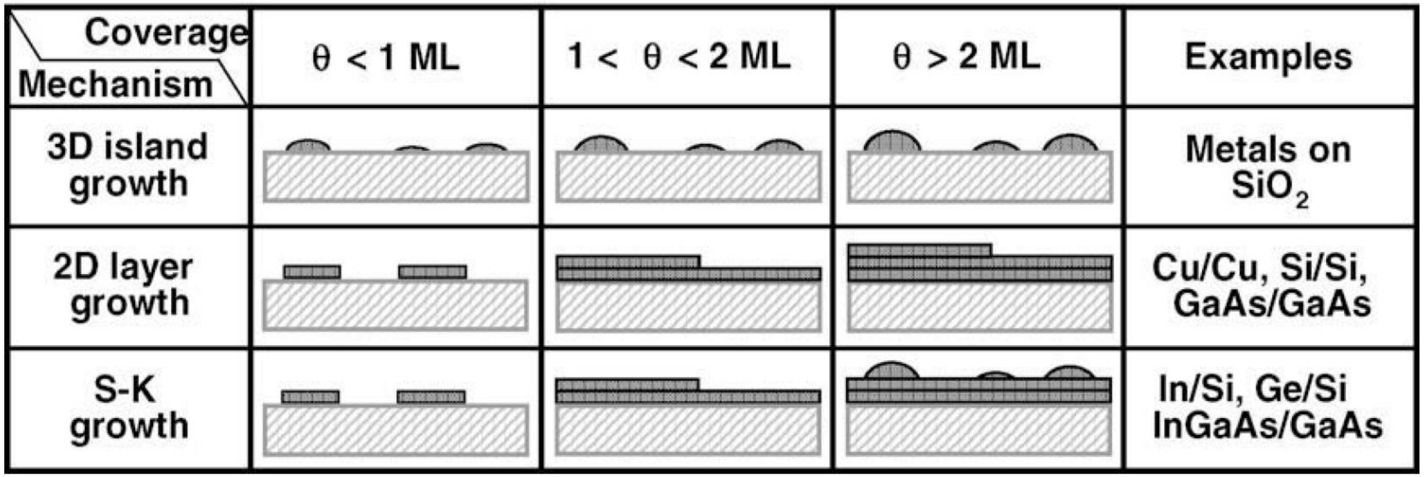
Growth modes



Coverage / Mechanism	$\theta < 1$ ML	$1 < \theta < 2$ ML	$\theta > 2$ ML	Examples
3D island growth				Metals on SiO_2
2D layer growth				Cu/Cu, Si/Si, GaAs/GaAs
S-K growth				In/Si, Ge/Si InGaAs/GaAs

Figure 12.1: Schematic representations of three solid-film growth modes on substrates. θ is the overlayer coverage in monolayers.

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Growth modes atomistic view

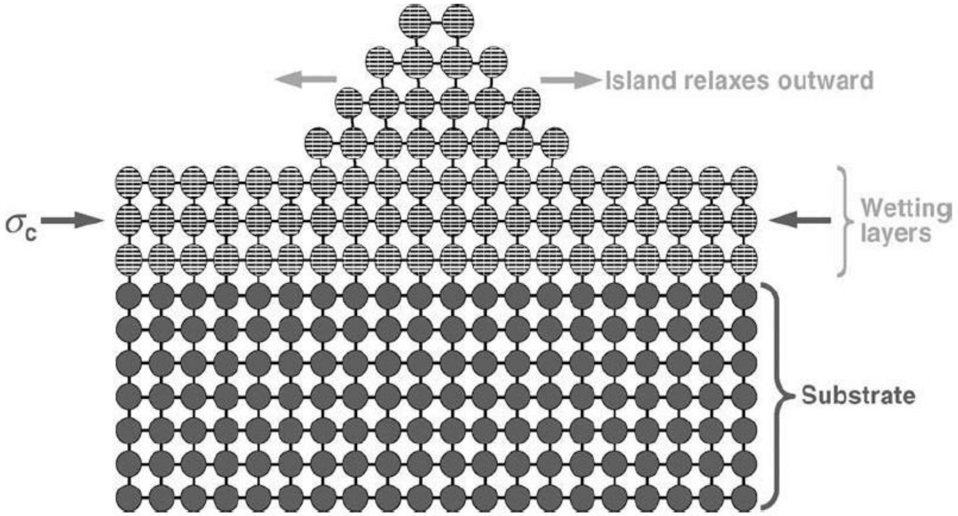

Figure 12.2: Schematic representation of strain-driven Stranski–Krastanow 'quantum dot' formation above an initial wetting layer. Here, the film lattice constant is larger than that of the substrate (i.e. $a_f > a_s$) and the layer is under compressive stress σ_c.

Growth modes atomistic view

An incident flux of film species must first become thermally accommodated with the substrate.

For a given adatom, this typically occurs within a few vibrational periods (even for sputtered atoms incident with several eV).

The adatoms then diffuse on the surface to interact with other adatoms or desorb (depending on film/substrate materials and Ts).

At sufficiently low temperatures, a fraction of the clusters which are formed continue to grow in size and become islands which eventually impinge on, and coalesce with, their neighbors to form a continuous film.

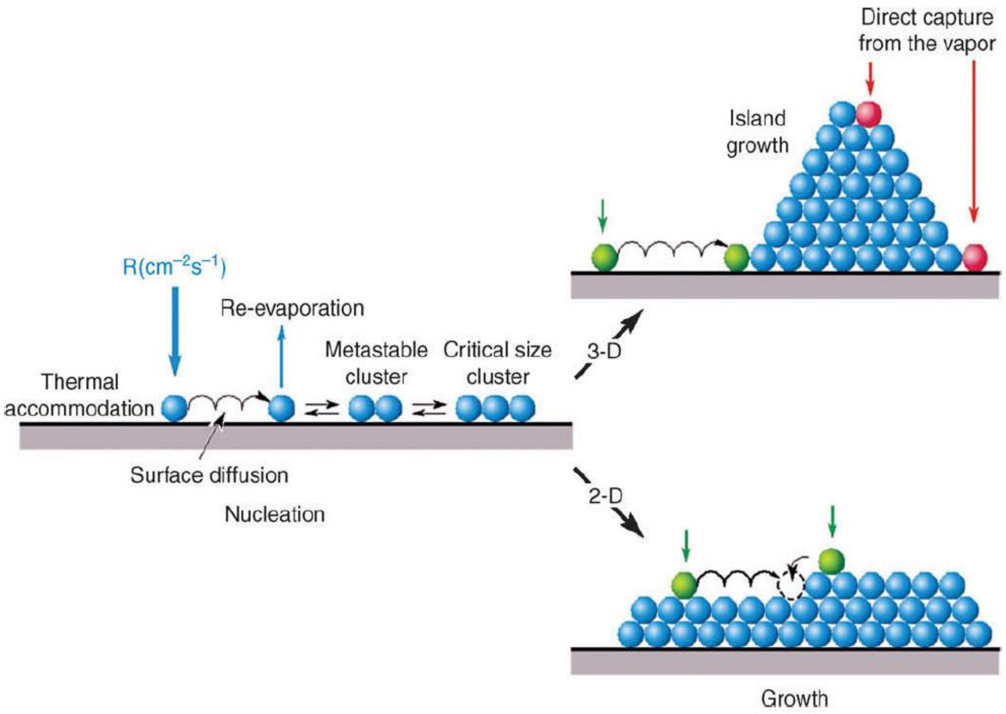

Figure 12.3: Schematic representation of processes leading to nucleation and 3D (upper right) and 2D (lower right) film growth.

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Kinetic processes in nucleation and growth

Among the questions addressed in this section are:

1. What is the **nucleation rate (N)** and how does it depend on time, temperature, deposition rate, and the nature of the film and substrate?

2. Once formed, what are the **possible mechanisms for subsequent growth and coalescence** of nuclei?

3. What is the **time dependence for the growth and coalescence of nuclei**?

In particular, distinctions between the macroscopic (e.g., capillarity) and microscopic (atomistic) views of these processes will be stressed.

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Nucleation rate

The **nucleation rate** is a convenient synthesis of terms that describes **how many nuclei of critical size** form on a substrate **per unit area, per unit time**.

Nuclei can grow through direct impingement of gas-phase atoms, but this is unlikely in the earliest stages of film formation when nuclei are spaced far apart. Rather, **the rate at which critical nuclei grow** depends on the **rate at which adsorbed monomers (adatoms) attach** to it.

vapor atoms which impinge on the substrate may immediately desorb but usually **they remain on the surface for a length of time** τ_s given by

$$\tau_S = \frac{1}{\nu} \exp\left(\frac{E_{\text{des}}}{k_B T}\right)$$

The vibrational frequency of an adatom on the surface is v (typically $10^{13} s^{-1}$) while E_{des} is the energy required to desorb it back into the vapor

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Nucleation rate

Adatoms, which have not yet thermally accommodated to the substrate, **execute random diffusive jumps** and may, in the course of their migration, **form pairs with other adatoms or attach to larger atomic clusters** or nuclei.

When this happens it is **unlikely that these atoms will return to the vapor phase**. This is particularly true **at substrate heterogeneities such as cleavage steps or ledges** where the binding energy of adatoms is greater relative to a planar surface.

The proportionately large numbers of atom bonds available at these accommodating sites leads to higher E_{des} values.

Thus a **significantly higher density of nuclei is usually observed near cleavage steps and other substrate imperfections**. The presence of impurities similarly alters Edes in a complex manner.

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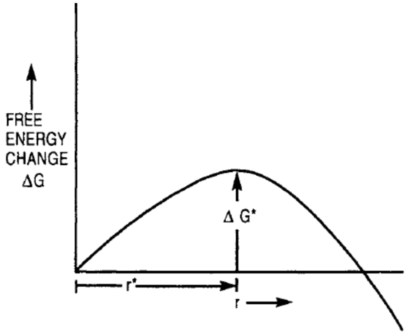
Nucleation rate

We now exploit some of these microscopic notions by noting that the nucleation rate N is essentially proportional to the product of three terms, namely,

$$\dot{N} = N^* A^* \omega \text{ (nuclei/cm}^2\text{-s).}$$

N* is the equilibrium concentration (per cm^2) of stable nuclei and **ω is the rate at which atoms impinge (per cm^2-s)** onto the nuclei of **critical area A*** (cm^2).

$$N^* = n_s \exp - \Delta G^*/k_B T,$$



Finally we would obtain after some transformations:

$$\dot{N} = 2\pi r^* a_0 \sin\theta \frac{PN_A}{(2\pi MRT)^{1/2}} n_s \exp\left(\frac{E_{des} - E_S - \Delta G^*}{k_B T}\right).$$

With Es activation energy of surface diffusion, Edes desorption energy of atom back to vapor, ns the density of nucleation sites

The **nucleation rate** is a very **strong function of the nucleation energetics** which are largely **contained within the term ΔG***.

$$\Delta G^* = \frac{16\pi(\gamma_{fv})^3}{3(\Delta G_V)^2}\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\}.$$

As noted earlier, a **high nucleation rate encourages a fine-grained or even amorphous structure** while a coarse-grained deposit develops from a low, value of $\dot{N}$.

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Ostwald ripening

Prior to coalescence there is a **collection of islands of varied size**, and with time the **larger ones grow or "ripen"** at the **expense of the smaller ones**. The desire to minimize surface free energy of the island structure is the drivingforce. To understand the process, consider two isolated islands of surface tension γ and different size in close proximity.

For simplicity they are assumed to be spherical with radii r1 and r2. The free energy (G) of a given island is

$$4\pi r_i^2\gamma$$

The island contains a number of atoms ni given by

$$4\pi r_i^3/3\Omega,$$

where Ω, is the atomic volume. Defining the free energy per atom μ_i or chemical potential as dG/dn~, after substitution

$$\mu_i = \frac{d(4\pi r_i^2\gamma)}{d(4\pi r_i^3/3\Omega)} = \frac{8\pi r_i\gamma dr_i}{4\pi r_i^2 dr_i/\Omega} = \frac{2\Omega\gamma}{r_i}.$$

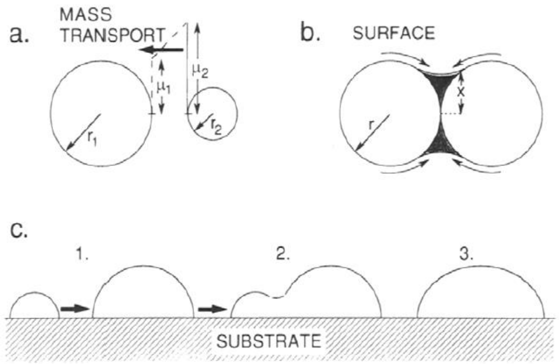

Figure 7-17 Coalescence of islands due to (a) Ostwald ripening, (b) sintering, (c) cluster migration.

Thus, if r1 > r2 **atoms will diffuse along the substrate from particle 2 (shrinking it in size) to particle 1** which grows at the former's expense. A mechanism has thus been established for coalescence without the necessity for islands to be in direct contact.

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Sintering

Sintering is a **coalescence mechanism involving islands in contact**.

Example: **Au particles** deposited on molybdenite (MoS_2)
at 400°C and photographed within the TEM.

Within **tenths of a second a neck forms between islands** and **then successively thickens** as atoms are transported into the region.

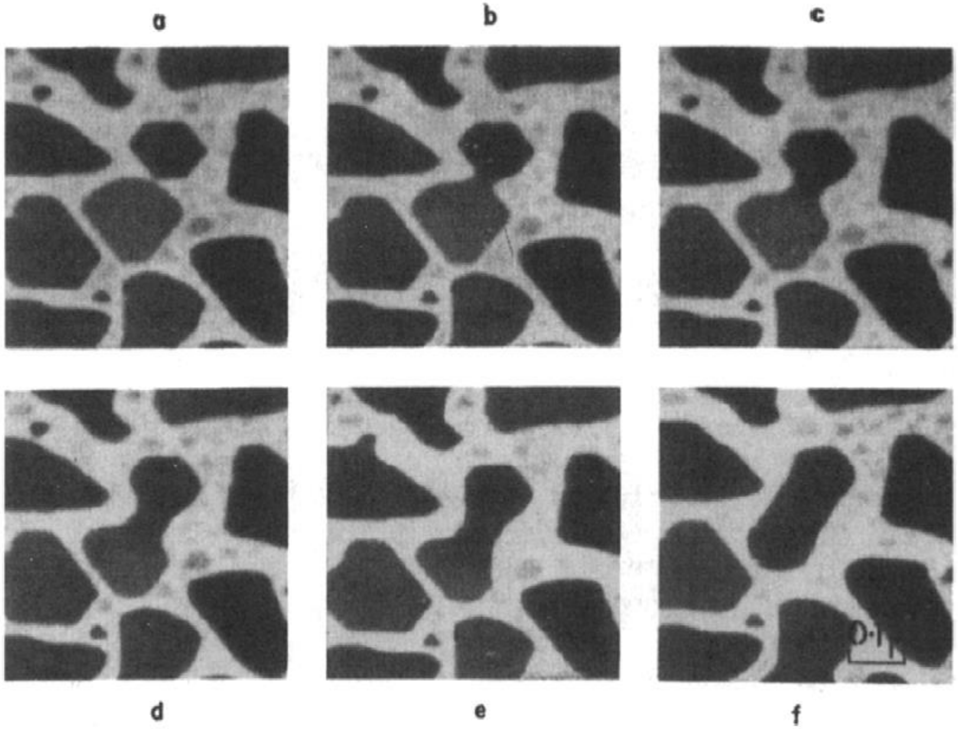

Figure 7-18 Successive electron micrographs of Au deposited on molybdenite at 400°C illustrating island coalescence by sintering. (a) Arbitrary zero time, (b) 0.06 s, (c) 0.18 s, (d) 0.50 s, (e) 1.06 s, (f) 6.18 s. (From Ref. 24.)

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Cluster migration

The last mechanism for coalescence considered deals with **migration of clusters on the substrate surface**. Coalescence occurs as a result of **collisions between separate island-like crystallites (or droplets) as they execute random motion**. Evidence provided by the field ion microscope, which has the capability of resolving individual atoms, has revealed the migration of dimer and trimer clusters.

Electron microscopy has shown that crystallites with diameters of ~ 50-100 A can migrate as distinct entities provided the substrate temperature is high enough. Interestingly, the mobility of metal particles can be significantly altered in different gas ambients.

Not only do the clusters translate, but they **have been observed to rotate as well as even jump on each other and sometimes reseparate thereafter**!

Cluster migration has been directly observed in many systems, e.g., Ag and Au on MoS2, Au and Pd on MgO, and Ag and Pt on graphite in so-called conservative systems, i.e., where the mass of the deposit remains constant because further deposition from the vapor has ceased.

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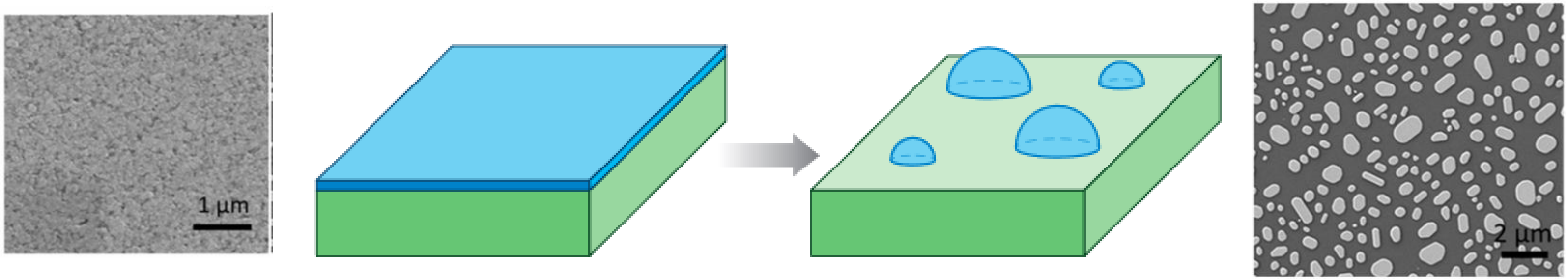
Dewetting in thin films

Solid-State Dewetting of Thin Films



During solid-state dewetting, thin films dewet to form isolated islands. This occurs while the material remains in the solid state.

- Thin films might dewet or agglomerate to form arrays of islands when heated.
- This can happen well below a **film's melting temperatures** so that dewetting (sometimes termed agglomeration) occurs while the film remains in the solid state.
- The driving force for dewetting is **minimization of the total energy of the free surfaces of the film and substrate, and of the film-substrate interface.**

Summary

- Sequence of events nucleation, growth and coalescence
- Island (Volmer-Weber), layer (Frank Van der Merwe), or Stranski-Krastanov nucleation mode
- Surface structure: atoms relax at the outer surface in a way to preserve in plane symmetry which leads to surface reconstruction
- 3 Surface energies: towards vapor phase around 1 J/m^2, Metals have highest, organic close to 100mJ/m^2
- Capillary theory: Gibb's free energy scales with r^3 and three interface contributions with r$^{2.}$ Mechanical equilibrium leads to Young's equation. The derivate=0 leads to critical radius of nucleus size r* and the nucleation barrier ΔG^*
- wetting factor dependent on Θ which has the value of zero for $\Theta = 0°$ and unity for $\Theta = 180°$. When the film wets the substrate, there is no barrier to nucleation. At the other extreme of dewetting, ΔG^* is maximum and equal to that for homogeneous nucleation.
- If γ_{fs} is neglected island growth occurs when the surface tension of the film exceeds that of the substrate
- The strain energy is relaxed in a 3D island, Therefore transition from 2D to 3D occurs beyond critical thickness of 2D layer (Stranski Krastanov growth). Atomistically the strained lattice planes can relay outwards in a 3D island.
- Higher substrate temperatures lead to increase in size of critical nucleus. Increasing the deposition rate leads to smaller islands
- Nucleation rate describes how many nuclei of critical size form per unit area and unit time. The rate at which critical nuclei grow depends on the rate at which adsorbed monomers (adatoms) attach, which is more likely at cleavage steps or ledges and depends strongly on ΔG^*.
- Ostwald ripening means larger islands grow or "ripen" at the expense of the smaller ones
- Sintering is a coalescence mechanism involving islands in contact.
- Cluster migration has been observed experimentally
- Dewetting might happen during annealing driven by minimization of surface energies at elevated temperatures

exercises

- What are the three basic growth modes
- What is a reconstructed surface?
- Derive the Young's equation. Start with a cross-section through a nucleus in form of a hemispherical cap. Explain the total wetting case.
- Explain the terms critical nucleus size and activation energy for nucleation. Denote both quantities in a free energy change vs nucleus radius plot.
- How does Stranski Krastanov Growth can be explained.
- Explain the term nucleation rate.
- Explain the difference between Ostwald ripening and sintering

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