Lecture one

Surface Energy and Nucleation Modes

1.1 Thermodynamic Nucleation Theory and Growth Modes

Formation of a crystal occurs through two processes mainly, nucleation and growth by condensation processes. Aggregation of the deposited species can form the so-called clusters, which can be either unstable or stable. Nucleation, which is the primary stage of the condensation, process from which growth proceeds, consists of random generation of solid-phase nanometer-size clusters that can irreversibly grow to macroscopically large sizes. In thermodynamics, nucleation originates from local fluctuations from equilibrium of a supersaturated starting phase that give rise to a phase transition (from the vapor or liquid to the solid phase). A supersaturated starting phase is a prerequisite for the occurrence of nucleation events [10]. Thermodynamically stable clusters, termed “nuclei,” form the building blocks of further condensation mechanisms (island growth, aggregation, and coalescence). From a thermodynamic standpoint, ***the key parameters controlling nucleation are***

1) the nucleation driving force, 2) the interface free energy, and 3) the condensation rate. ***To describe the thermodynamic equilibrium state and growth morphology*** *of the supported thin film*, 1)the wetting conditions, 2)the supersaturation, and 3) the degree of misfit between the

film and the substrate are the main parameters to be considered. The final morphology is the result of the growth mode adopted from the deposit. The main thermodynamic growth modes are the layer-by-layer growth (2D growth), island growth (3D growth), and the mode starting out as layer-by-layer growth followed by island formation. They are determined by the competition between surface and interface free energy, as well as the competition between strain energy and strain relief [43,44].

1.2 Principles of Nucleation Theory

The main concepts concerning nucleation in phase transformations of a fluid phase within another fluid were introduced by Gibbs, which considered ensuring minimal free energy with respect to the radius as the thermodynamic criterion to form nuclei [45]. The radius satisfying such a condition was termed "critical nucleus radius." Although oversimplified, Gibbs's picture introduced some key assumptions that were later transferred to model the nucleation of crystals from dilute or condensed fluids or from other solid states [46, 47, 48, 49]. The basic formulation of classical nucleation theory dates to 1927 by Volmer, Weber, and Farkas [50,51] and to 1935 by Becker and Döring [52]. Thermodynamically, a nucleation process was modeled as the formation of small embryos of the new homogeneous phase inside a large volume of the old phase (parent phase) due to heterophase fluctuations [53,54].

The temperature was the controlling parameter driving the transition of an initially stable (at thermal equilibrium) homogeneous phase to a metastable state, that is, stable with respect to small and unstable with respect to sufficiently large thermal fluctuations. In other words, the transformation required overcoming a free-energy barrier ΔG^* termed "nucleation barrier" [11, 55, 56]. In the framework of the so-called homogeneous capillary approximation [50, 51, 52], the main assumption was that the cluster free energy to be minimized with respect to the size can be partitioned as the sum of surface and volume contributions. According to such a classical thermodynamic picture, the stability of clusters depends on the balance between the surface and volume free energies that contribute to the formation of free energy. This is easily understood by considering the free-energy changes associated with the formation of a spherical cluster with a radius r from an old phase whose free energy has become higher than that of the emerging bulk new phase. The condensation reaction is driven by the chemical free-energy change per unit volume. A cluster containing units (termed "monomers"), each occupying a volume V, is composed of $(4/3)лr^3/V$ units. Hence, thermodynamically, forming a spherical cluster with a radius r involves a change of Gibbs free energy ΔG_V or a volume energy $\Delta\mu_v$ given by

$$\Delta\mu_V = (4/3)лr^3\Delta G_V.$$

In the case of condensation from a supersaturated initial phase

$$\Omega\Delta G_V = -[(k_B T)\ \ln\ (1 + SS)], \tag{1.1}$$

where Ω is the atomic volume and SS is the already defined supersaturation ratio. The energy reduction $\Delta\mu_V$ is counterbalanced by an increase in the surface energy $\Delta\mu_S = 4\pi\gamma r^2$, wher γ is the surface energy per unit area. Then, the total change of the chemical potential (i.e., the difference of chemical potentials in the parent and in the nucleating equilibrium phases) [31,55] resulting from the formation of a cluster of radius r defines the free energy ΔG associated with the formation of a solid spherical cluster in an otherwise homogeneous fluid:

$$\Delta G = \Delta\mu_V + \Delta\mu_S = (4/3)\pi r^3 \Delta G + 4\pi\gamma r^2 \tag{1.2}$$

In thermodynamics the change in free energy associated with the formation of a cluster is also called work of formation. The general profile of the change of volume free energy $\Delta\mu_V$, surface free energy $\Delta\mu_S$, and the formation energy ΔG is shown in Fig. 1.2 as a function of cluster radius. The surface contribution to the free energy is always positive and acts to destabilize the cluster—the more unstable the cluster is the larger its surface-to-volume ratio is. Once the size r gets large enough, the drop in the free energy associated with the formation of the bulk phase dominates the surface free energy and every further increase of size lowers the free energy of the system. From there on, the gain in volume drives the growth of a cluster because growth becomes energetically favorable.

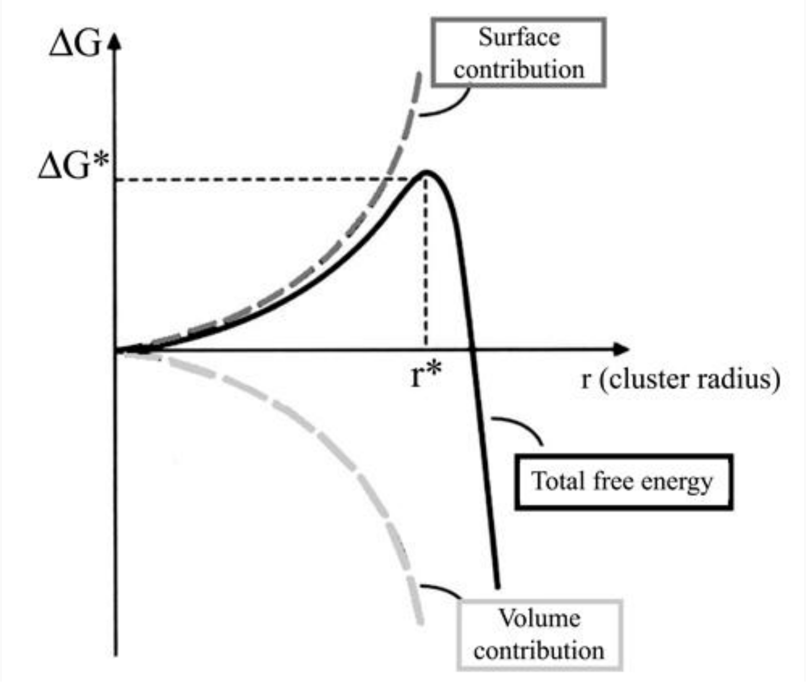

Figure 1.2 General profile of the change of the volume free energy, surface free energy, and formation energy in a nucleation process in the thermodynamic framework.

Because of the competition between the volume and the surface contributions, the formation energy ΔG shows a maximum ΔG* at a cluster radius r*, usually termed "nucleus critical size." The formation of a cluster with a critical size (the one for which the free energy ΔG is maximum) is referred to as nucleation. The expressions of ΔG* and r* can be easily estimated by setting equal to zero $(d\Delta G/dr)|_r$ = r*, solving which gives the following formulas [57]:

$$\Delta G^* = (16.\pi r^3)/3(\Delta G_V)^2 \qquad (1.3)$$

$$r^* = 2\gamma/\Delta G_V \qquad (1.4)$$

As the maximum value of the formation energy (ΔG*) represents an energy barrier that a nucleation process must overcome to form an irreversibly growing nucleus, it is called activation energy for nucleation or nucleation barrier. The dependence of both ΔG* and r* on the surface free energy has the important implication that any change of the surface free energy affects the cluster formation. Therefore, below the critical size r* the surface term $\Delta\mu_S$ dominates the volume contribution $\Delta\mu_V$ and drives the increase of the energy of the growing clusters (Fig. 1.2). As a result, a cluster of radius r < r* (termed subcritical cluster) is unstable, that is, once formed, it will tend to disintegrate in monomers and/or smaller clusters. Instead, since above the critical size r*, the drop in free energy is dominated by the volume term ΔμV, a cluster larger than r* will continue to grow. A cluster with a size at least equal to the critical size is usually termed "nucleus" or "supercritical cluster."

The nomenclature "homogeneous nucleation" is adopted to refer to a cluster formed within a homogeneous phase. In the presence of an additional foreign material acting as a catalyst for the cluster formation (heterogeneous nucleation), the formation energy ΔG is expressed in terms of the interface energy related to the cluster surface ($\gamma_{cluster}$), the substrate surface (γ_{sub}), and the cluster–substrate interface ($\gamma_{cl\text{-}sub}$). Under the assumption that a hemispherical (spherical cap-shaped) cluster of radius r is formed over a substrate, it results in:

$$\Delta G = \Delta\mu_V + \Delta\mu_S = a_1 r^2 \gamma_{cluster} + a_2 r^2 \gamma_{cl\text{-}sub} - a_2 r^2 \gamma_{sub} + a_3 r^3 \Delta G_V, \qquad (1.5)$$

where the coefficients are geometric factors, with a_1r^2 the surface area, a_2r^2 the projected surface area, and a_3r^3 the volume of the spherical cap-shaped cluster. The same procedure applied in the case of the homogeneous nucleation lets us obtain the following expressions of the critical nucleus size r* and the maximum formation energy

$$r^* = -2(a_1\gamma_{cluster} + a_2\gamma_{cl\text{-}sub} - a_2\gamma_{sub})/3a_3\Delta G_V \qquad (1.6)$$

$$\Delta G^* = 4(a_1\gamma_{cluster} + a_2\gamma_{cl\text{-}sub} - a_2\gamma_{sub})^3/27(a_3\Delta G_V)^2 \qquad (1.7)$$

The above thermodynamic formalism provides a generalized framework that lets us include in a straightforward way other energy contributions such as strain. In the presence of a lattice mismatch between depositing material and substrate, a term proportional to $r^3\Delta G$ strain, where

ΔG strain is the strain free-energy change per unit volume, must be inserted in the formation energy ΔG leading to an increase of the overall energy barrier to nucleation ΔG^*. Stress relief occurring during nucleation favors a reduction of ΔG^*. To summarize the classic thermodynamic picture, clusters smaller than a critical size appear and disappear spontaneously through thermal fluctuations. A transient regime, lasting a time termed “incubation time,” exists before the nucleation rate reaches its stationary value [55, 58, 59, 60]. In the case of a nucleation barrier comparable to or higher than the thermal energy k_BT, metastable clusters may overcome the critical size and from there on continue to grow and become more and more stable. Classical nucleation theory assumes that the steady-state distribution of a nucleating system slightly deviates from the equilibrium distribution around the critical size. Cluster random size fluctuations around the critical size may cause disintegration of a stable nucleus [52] and only the critical clusters reaching a size large enough to enter the steady-state regime fall in the stable region and can continuously grow (supercritical nuclei). Definitively, the steady state can be reached once the cluster size increases far enough away from the critical size.

An important property of the activation energy ΔG^* is its strong influence on the density of stable nuclei. As in the case of any kinetically limited process, classical nucleation theory assumes that the nucleation probability or rate J (i.e., the number of nuclei formed per unit time per unit volume) obeys an Arrhenius law. That is, supercritical nuclei generate due to thermodynamic fluctuations in the subcritical region by overcoming the nucleation barrier ΔG^* at a rate $J = J_o\exp(-\Delta G^*/k_BT)$ [31,61]. The prefactor Jo also depends on the supersaturation ratio SS, material constants, and temperature, as well as fluctuations around the critical size by the nonequilibrium Zeldovich factor [52]. Therefore, a high nucleation barrier would involve a small concentration of critical nuclei. Notably, the Zeldovich expression for the nucleation rate implies that J is relatively very small until a critical value of SS is achieved, after which J increases exponentially. Furthermore, the values of both r^* and ΔG^* decrease for increasing SS [62]. If SS is high enough, the nucleation barrier would virtually vanish and the rate of formation and growth becomes limited by the rate of transport of mass or energy. Classical nucleation theory assumes a not too high SS, that implies a large enough critical size. This assumption also has procedure implications because it allows one to treat the cluster size as a continuous variable and introduce derivatives to minimize ΔG as well as make a finite expansion of key quantities around the critical size. The dependence of the nucleation rate J on the nucleus critical size implies that the nucleation process can be operatively affected by modulating the critical size, for example, through the interfacial energy. In the case of heterogeneous nucleation, the decrease in the value of the surface free energy favors decrease of r^*, ΔG^*, and critical supersaturation [62]. Therefore, under conditions of low SS heterogeneous nucleation is energetically more favored than homogeneous nucleation. On the other hand, it may be energetically favored for the clusters to form heterogeneously on preferred nucleation sites (such as steps, dopant sites, existing impurities, or some lattice defects) than homogeneously because of their acting as catalyzers in lowering the cluster free energy by a gain in the interface free energy. In general, heterogeneous and homogeneous nucleation can compete with each other depending on the number of heterogeneous sites with respect to the total number of sites for homogeneous nucleation. As a result, nucleation can be manipulated by tuning either the supersaturation or the nucleation environment.

As a concluding remark, the main conclusions of classical nucleation theory can be derived as approximated solutions of a kinetic approach that solves for a master equation to describe the nucleation process and model the dynamics of the cluster size distribution (population) [52, 60, 63]. Moreover, to describe the nucleation evolution (nucleation and its whole kinetics) an approach was developed that couples classical descriptions and kinetic approach [64]. In the framework of the cluster dynamic model, a cluster is defined by a single parameter, that is, its size or the number of units it contains. The cluster dynamic formulation removed two limiting assumptions of the classical nucleation theories: first, the assumption that only reactions involving monomers can occur and, second, the assumption that the cluster composition is given (i.e., the nucleating phase at equilibrium with the parent phase). Whenever this information is not known a priori, other modeling techniques can be applied, such as molecular dynamics [65,66] and kinetic Monte Carlo simulations [67]. Over the years, the “kinetic theory” of homogeneous nucleation has been revised and/or extended [68, 69, 70]. Discussions of the conceptual differences between cluster dynamics and classical nucleation theory have evidenced consistency between the results of the two approaches in the dilute limit and coherence concerning the critical size in the limit of large cluster sizes [71, 72, 73]. These findings underline some limitations of the classical approach with increasing supersaturation [66]. Indeed, the classical nucleation approach fails in the limit of a very small critical nucleus because of the increased weight of the surface free-energy term and the influence of the sharp curvature on the interfacial energy [74].

1.3 Growth Modes at Thermodynamic Equilibrium

Thermodynamic arguments let us introduce a recipe to describe the equilibrium form of a crystal A condensed on a crystal B (acting as a substrate) in terms of the interfacial free energy γ_{AB} between A and B in addition to the surface free energies γ_A and γ_B of the crystals A and B, respectively. In the following, on the basis of the nomenclature usually adopted experimentally, γ_A and γ_B will be called γ_{film} and γ_{sub}, respectively, where the subscripts “film” and “sub” stand for film and substrate, respectively. Also, γ_{AB} will be referred to as $\gamma_{interface}$. Historically, the attempts to understand and predict the epitaxial growth based on thermodynamics depicted three main scenarios named after their original investigators: the Frank–van der Merwe (FM) growth mode (i.e., 2D morphology, layer-by-layer growth, or step-flow growth) [75], the Volmer–Weber (VW) growth mode (i.e., 3D morphology, island growth) [50], and the Stranski–Krastanow (SK) growth mode (i.e., initially 2D morphology evolving toward a 3D morphology after a critical thickness, layer-plus-island growth) [76].

Unification and more rigorous treatment of the classification of the thermodynamic growth modes in heteroepitaxy was achieved by introducing the so-called wetting factor [9]

$$\Phi = \gamma_{\text{film}} + \gamma_{\text{interface}} - \gamma_{\text{sub}}. \tag{1.8}$$

According to the competition between surface and interface energies

(i) if $\gamma\mathrm{film} + \gamma\mathrm{interface} \leq \gamma\mathrm{sub}$, then a pure 2D layer-by-layer growth results (FM growth mode) (Fig. 1.3a);

(ii) if $\gamma\mathrm{sub} < \gamma\mathrm{film} + \gamma\mathrm{interface}$, then a 3D morphology is energetically favored (VW growth mode) (Fig. 1.3b); and (iii) in the presence of strain, the relationship $\gamma\mathrm{film} + \gamma\mathrm{interface} \leq \gamma\mathrm{sub}$ implies a crossover from layer-by-layer 2D growth to 3D island growth ($\gamma\mathrm{film} + \gamma\mathrm{interface} > \gamma\mathrm{sub}$) at a critical thickness of the deposit (SK growth mode) (Fig. 1.3c).

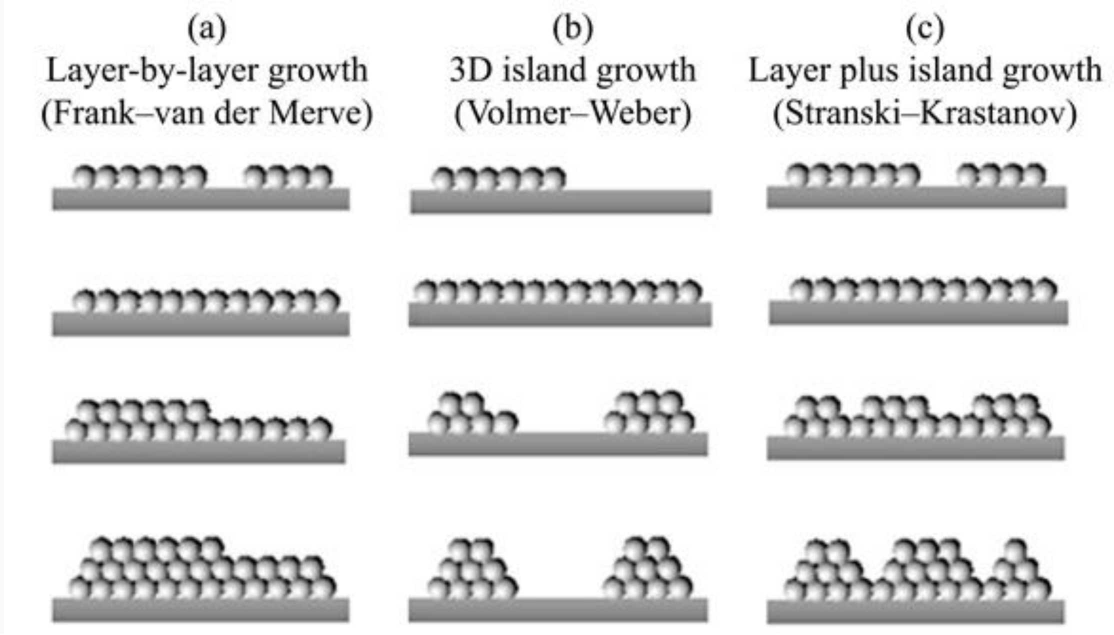

Figure 1.3 Morphology evolution (from top to down) leading to the three fundamental thermodynamic growth modes in heteroepitaxy (from the left, the Frank–van der Merwe growth mode, the Volmer–Weber growth mode, and the Stranski–Krastanow growth mode).

The above classification of the thermodynamic growth modes based on the wetting factor $\Phi = \gamma_{film} + \gamma_{interface} - \gamma_{sub}$ (2D growth for $\Phi < 0$ and 3D growth for $\Phi > 0$) doesn't account for the surface stress effects. Thermodynamics of strained solids and surface thermodynamics have been developed for describing thermodynamic transitions and crystal growth in the presence of epitaxial strain [23, 33, 77] and to connect the surface stress to the surface energy [78,79]. In general, the epitaxial stress acts against wetting, hence leading to a thickening and morphology evolution toward a 3D equilibrium shape [80,81]. If an inhomogeneous strain is disregarded that can create preferential sites for 2D or 3D nucleation, the interplay between thermodynamics and elastic effects allows the discussion of the thermodynamic classification of the main growth mechanisms, as follows. Whenever the sum of the surface free energy of the film and the interface free energy is lower than the free energy of the substrate surface (i.e., $\Phi < 0$), the gain of energy results from the complete coverage of the substrate by the film that thickens uniformly in a pure 2D layer-by-layer manner (FM growth mode) (Fig. 1.3a). The equality in equation $\gamma_{film} + \gamma_{interface} = \gamma_{sub}$ holds for the trivial case of homoepitaxy, where the interface between film and substrate essentially vanishes ($\gamma_{interface} = 0$). Since the surface energy of a crystal depends mainly on the chemical bond energies, the layer-by-layer growth mode is thermodynamically favored when the species of the overlayer can be more tightly bound to the substrate than to each other and bonding dominates surface diffusion [82]. Under this circumstance, the deposited material nucleates on the substrate surface, forming 2D islands, which coalesce with increasing coverage, and then the first complete monolayer on the substrate surface becomes covered with a somewhat less tightly bound second layer (Fig. 1.3a). This growth evolution provides a layer-by-layer growth mode, meaning that a layer is completed before nucleation of a new layer starts. In practice, however, nucleation on higher layers starts before the previous layer has been completed, thus forming steps responsible for a transient roughening. In fact, the surface morphology of the growing crystal changes from smooth over rough by nucleation of 2D islands to smooth by coalescence of 2D growing islands that form a layer without steps. If the film and substrate materials are lattice mismatched, the 2D growth can continue until the epilayer is able to accommodate elastically the building up (compressive or tensile) strain. In the case $\Phi = 0$, a film grown onto a rigid substrate is stable, provided its thickness is smaller than some critical value depending on the supersaturation [83]. Wetting interactions with $\Phi < 0$ and relief of surface stress can act to stabilize again the film up to a larger thickness [84]. As the accumulated strain energy increases linearly with the thickness of the epilayer, relief of the strain energy can cause the formation of interfacial misfit dislocations for thick (above a critical thickness) films having a small lattice misfit with respect to the substrate. For higher misfits, the growth mode changes to the layer-plus-island SK mode (Fig. 1.3c). Therefore, a layer-by-layer growth mode is the situation occurring in heteroepitaxy if the free-energy minimum of the growing deposit favors an atomically smooth surface. It is observed in the case of rare gases adsorbed on graphite and on several metals, in some metal-metal systems, and in semiconductor growth on semiconductors. The layer-by-layer growth is technologically important for depositing quantum well heterostructures and superlattices by epitaxial growth.

When the surface free energy of the film plus the substrate surface free energy is lower than or comparable to the interface free energy, a partially covered substrate surface is energetically more favorable than the growth of a uniform epilayer (VW growth mode) (Fig. 1.3b). The role of the strain must be also taken into account. While the deposition of material starts with a complete wetting of the substrate (a so-called wetting layer forms), as the deposition progresses strain energy accumulates with increasing thickness of the wetting layer and drives the system to enter a metastable region (i.e., there is a potential for 3D growth with an activation energy or barrier to be overcome). For lattice-mismatched film-on-substrate systems, as the elastic strain energy increases linearly with the film thickness and quadratically with the strain, the formation of coherent 3D islands is energetically favored beyond a critical thickness to release the strain energy. If this one begins to build up as the first few atomic layers wet the substrate, once the wetting layer reaches a critical thickness it decomposes and the growth proceeds with the formation of self-assembled 3D islands (clusters larger than a critical size) (Fig. 1.3b) that grow steadily determined by surface and interface energies and bond strength. In this respect, the island growth mode is associated with the situation where the species of the epilayer are more strongly bound to each other than to the substrate. Once small 3D clusters are nucleated directly on the substrate surface, they grow into islands of the condensed phase because nearly vanishing second-neighbor bonds (as in the case of the edge atoms of a 3D island) involve a rough surface as the lower-free-energy surface. Therefore, in heteroepitaxial growth on a lattice-mismatched substrate, the equilibrium shape (3D islands) is determined by the minimization of the total energy (including the strain contribution) rather than the minimization of the surface energy. The VW growth mode is usually observed in heteroepitaxial systems for strained layers with a lattice mismatch larger than 10%, for example, in the case of many systems of metals growing on insulators [85, 86, 87, 88, 89], alkali halides, graphite, and compounds such as mica.

The SK growth mode is an interesting intermediate hybrid growth mode governed by elastic relaxation [90]: after a wetting layer a few nanometers thick forms, subsequent layer-by-layer growth is unfavorable and an island forms over the wetting layer. The condition $\gamma_{film} + \gamma_{interface} \leq \gamma_{sub}$ implies instability at a critical thickness t_c (depending on strain and chemical potential), where a switch to the relationship $\gamma_{film} + \gamma_{interface} > \gamma_{sub}$ drives a crossover from 2D to 3D growth morphology (Fig. 1.3c). From the standpoint of the chemical bond energies, in the case of strong bonding to the substrate of the film species, the growth of one or more monolayers is favored energetically at the beginning. However, as this interaction is over a short range, subsequent evolution to a cluster morphology occurs energetically, driven by a mismatch in the lattice parameter or symmetry or crystal orientation between the bulk material of the epilayer and the substrate. Morphology transition is favored by the accommodation of elastic strain in a pseudomorphic layer that changes the balance between the surface and interface free energies during growth. Notably, the formation of islands on top of a thin wetting layer may be coherent, that is, dislocation free.

According to thermodynamics, the net free-energy change for the nucleation of a hemispherical island with a radius r assumed to be incoherent (or relaxed) on top of a growing, strained partially relaxing epilayer is given by

$$\Delta G = \Delta\mu_V + \Delta\mu_S = (2/3)\pi r^3 \Delta G + 4\pi\gamma r^2 + \Delta G_{\mathrm{strain}}, \qquad (1.9)$$

where ΔG is the volume free energy of the island, γ is the interface free energy, and the strain energy interaction between the island and the underlying epilayer ΔGstrainrepresents the difference in epilayer strain energy per unit area after the island nucleation (l/2Yε2) relative to that in the epilayer prior to island nucleation [91]. On the basis of the theory of elasticity, the epilayer strain energy Gstrain before and after the island nucleation can be written as l/2Yf2 and l/2Yε2, respectively, where Y is the elastic modulus of a layer and ε/f is its strain and f is the lattice mismatch strain defined as f = (asub – afilm)/afilm (afilm and asub being the lattice parameter of film and substrate, respectively). Under the condition that ΔG has a minimum with respect to r and in the limit of a vanishing critical radius, the critical thickness of the wetting layer can be evaluated as given by tc = 2γ/[(ε2 – f2)Y]. This the thickness of the epilayer for the onset of the rough island morphology (e.g., SK growth) [13].

Therefore, in the case of strained epitaxy, the system undergoes a transition from 2D to 3D island growth mode due to interplay between second-neighbor bond strengths and strain energy that both dictate the deposit equilibrium morphology. In this case the lattice mismatch is commonly a few percent compressively strained. The SK growth mode can be observed in semiconductor/metal systems such as Ge/Si(001), InAs/GaAs, CdSe/ZnSe, GaN/AlN, Bi/GaP, Ag/Si, Au/Ni, and Au/Ag. For example, since the lattice constant of Ge is 4.2% larger than that of Si, while growing a Ge/Si(001) system a Ge wetting layer consisting of about 4–5 monolayers can be grown before 3D Ge islands form with sizes of tens of nanometers on its topmost surface. The SK growth mode is applied for fabricating coherently strained 2D systems, as well as arrays of closely spaced quantum dots with control on size and shape dispersion [92].

Definitively, the growth regimes of a film can be classified in terms of surface energy ratio W = (γsub – γfilm)/γsub as a function of the lattice misfit, leading to a plot of the stability regions of the three main growth modes: island growth dominates in the case of W < 0 and layer growth is possible only when W > 0 and in the presence of a small amount of misfit (strained-layer epitaxy). In between and in competition with the island growth mode and layer morphology is the layer-plus-island SK growth mode. The energy stored in an interface between epitaxial film and substrate is determined by the relative contributions of elastic strain (deformation of the lattice of the film) and formation of edge dislocations.

1.4 Elementary Kinetic Processes on Surfaces and the Energy Landscape

The thermodynamic approach to growth lets one predict the close-to-equilibrium growth modes. However, the applicability of the thermodynamic classifications to modern growth experiments is limited because most deposition experiments are performed under far-from-ideal equilibrium conditions. Therefore, growth is ruled by kinetic parameters and processes, as well as a complex energy landscape. This section deals with the elementary processes occurring on a substrate surface, during and following deposition of species, that concur to the growth stages and structure formation. The characteristic kinetic parameters and laws governing such processes and the corresponding nomenclature will be introduced and discussed [93]. The main independent experimental variables effective in tuning the growth regimes are the substrate temperature (T_{sub}), the deposition flux F (the number of impinging species per unit surface area and per unit time), and the kinetic energy of the deposited species that strongly depends on the method used to generate the deposition flux (e.g., thermal evaporation, sputtering, and laser ablation). During growth, the substrate temperature influences the surface diffusivity of the adsorbed species, as well as residence time and condensation processes. In growth mechanisms, the surface mobility, which plays an important role in determining the growth modes, can also be influenced by the energy of the deposition flux. Typically, the deposition kinetic energies are of the order of 0.5–1 eV for the evaporated species, hundreds of electron-volts for the sputtered species, and hyperthermal energies (10–100 eV) in the case of laser-ablated species [18]. In experiments of deposition from the vapor/gas phase, the actual deposition flux F is related to the supersaturation ratio SS by the relationship $SS = k_B T \ln(F/F_0)$, where k_B is the Boltzmann constant, T is the absolute growth temperature, and F_0 is the equilibrium value of F at the temperature T [10,18]. Thermodynamic growth conditions (so-called close to equilibrium) are associated with small or moderate SS and/or a high T_{sub}.