29 Semiconductor Quantum Dots: Model Case Ge/Si

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29.1 Introduction

During the past few decades, the field of nanoscience and nanotechnology has undergone a revolution that parallels the extraordinary advances in surface science instruments and techniques. The nano-era is posited as having begun in the early 1980s with the invention of scanning probe microscopy which allowed one to monitor, measure, and manipulate matter at the nanoscale level. Dramatic new insights have come from the application of this and other new experimental tools. The ability to precisely control atoms and build molecules at extremely small length scales is leading to unprecedented breakthroughs in electronics [1, 2], photonics [3, 4], medicine [5], and energy production [6].

In particular, the formation of periodically ordered structures offers the possibility of direct fabrication of semiconductor quantum nanostructures in which a narrow gap material is embedded into a matrix of a wide-gap material providing a confined potential for carriers. Periodic structures of such inclusions create a superlattice comprising quantum wells, quantum wires, and quantum dots (QDs). QDs, the ultimate limit of low-dimensional structures, have become a fascinating subject both for the basic research and for device application.

The most powerful and common method to obtain high-quality QDs consists in exploiting the Stranski–Krastanov (SK) growth mode during strained heteroepitaxial growth, in which QDs spontaneously form on top of a thin wetting layer (WL). A prototype system for studying the fascinating and complex phenomena related to the strain-driven heteroepitaxy and for investigating the properties of QDs' spontaneous formation is Ge/Si. As a model system, Ge on vicinal Si(001) makes it possible to investigate strain relaxation, growth instabilities, and three-dimensional (3D) island formation and self-organization. Moreover, by changing the substrate miscut, it is possible to tune both the energetic and the kinetic factors governing the growth of single nanostructures [7].

There is a huge literature on the SK growth of Ge on Si surfaces and many excellent monographs and review papers surveying the different aspects of the subject have been written [7–11]. Most of them are aimed at researchers with some

Surface and Interface Science: Solid-Solid Interfaces and Thin Films, First Edition. Edited by Klaus Wandelt. © 2014 Wiley-VCH Verlag GmbH & Co. KGaA. Published 2014 by Wiley-VCH Verlag GmbH & Co. KGaA. preliminary knowledge on the matter, whereas it is rather difficult to find a concise handbook providing a unified picture to connect the experimental trend with the basic knowledge on nucleation, crystal growth, and theory of epitaxy.

This chapter is intended neither as a comprehensive overview of all the growth nor as a survey of the methods employed to investigate and characterize semiconductor nanostructures. Its purpose, rather, is to present an original connection between the physical mechanisms at the origin of nanostructure formation and the basic principles of nucleation and epitaxial growth theory. We aim to provide an introductory guide, easily accessible to nonspecialized readers, to tackle the fundamental ingredients involved in the epitaxial growth of Ge/Si semiconductor QDs (e.g., substrate symmetry, bulk/surface elastic energy balance, and intermixing). The idea is to connect the factors that play an important role in the growth process to the fundamentals of nucleation theory, thereby providing a general purpose tool that can be applied to similar systems such as the III-V heteroepitaxial growth of nanostructures. For this reason, we deliberately avoided including details that could not be extended to similar systems. The reader interested in further discussion may refer to the excellent specialized review papers listed in the reference section. Also, we have chosen, whenever possible, an analytical approach the reader can actually follow without accepting it as given. This sometimes has required a simplified mathematical treatment and modeling with respect to up-to-date literature, but preserves the physical meaning underneath.

The chapter is organized as follows: after an introductory section in which the basic concepts and definitions are specified, the classical Bauer's classification of the epitaxial growth modes is examined, extending to a generalized thermodynamic criterion for the mechanism of growth in Sections 29.2. The equilibrium shape of 3D dots grown on a flat substrate of different lattice constant is the subject of Section 29.3. In Section 29.4, the effect of the substrate morphology is handled: in particular, how much the substrate vicinality can produce a fine shaping of GeSi nanostructures is studied in agreement with the experimental results. To get over the elastic relaxation, in Section 29.5, the influence of intermixing on QD nucleation is considered. Finally, in Section 29.6, we address an issue regarding nanotechnology applications, namely, the elastic interaction between Ge islands on vicinal Si substrates and its effect on the lateral ordering of nanostructures.

29.2 Thermodynamic Criterion of the Growth Mode

29.2.1

Epitaxial Growth: Basic Concepts and Definitions

The word epitaxy derives from the Greek prefix *epi* meaning "upon" or "over" and *taxis* meaning "arrangement" or "order" and refers to the oriented growth of a crystalline material on the single crystal surface of a different material. The term was coined by Royer [12] in 1928 to distinguish the phenomenon of epitaxial growth



Figure 29.1 Schematic representation of the three primary modes of thin-film growth according to Bauer's classification: (a) Frank-van der Merwe (FM) or layer-by-layer mechanism; (b) Volmer–Weber (VW) mechanism or island growth; and (c) Stranski–Krastanov (SK) or layer-by-layer followed by island growth.

from the usual crystal growth that occurs when a single crystal film is grown on the surface of the same material. Strictly speaking, epitaxial growth takes place when deposit and substrate crystals differ chemically or geometrically owing to the nature and strength of the chemical bonds, on one hand, and the crystal lattice structures, on the other. From a thermodynamic standpoint, this means that both substrate and deposit crystals have different chemical potentials. Furthermore, it also means that the chemical potential of the growing epilayer $\mu(n)$ varies with the film thickness *n* and differs from that in the bulk deposit crystal ($\mu(n) \neq \mu_{\infty}$), because of the interaction with the substrate. As will be shown in the following sections, the thickness dependence of the chemical potential defines a thermodynamic criterion [13–16] for the mechanism of growth of epitaxial films, which is equivalent to that given by Bauer [17] in terms of the specific surface energies. Following Bauer's approach, the mode of epitaxial growth is classically discussed on the basis of the interrelation of the specific free surface energies of the deposit (σ), the substrate (σ_s) , and the substrate-deposit interface (σ_i) . Layer-by-layer growth or *Frank-van* der Merwe (FM) mode (Figure 29.1a) is expected when the change in surface energy accompanying the deposition process $\Delta \sigma = \sigma + \sigma_i - \sigma_s$ is negative, namely

$$\sigma_{\rm s} > \sigma + \sigma_{\rm i} \tag{29.1}$$

Conversely, in the case of incomplete wetting or Volmer-Weber (VW) mode

$$\sigma_{\rm s} < \sigma + \sigma_{\rm i} \tag{29.2}$$

the film grows as isolated 3D islands (Figure 29.1b). Layer-by-layer followed by 3D islanding (Figure 29.1c), or SK mechanism, takes place when $\Delta\sigma$ changes sign from negative to positive after some characteristic thickness due to the misfit strain energy accumulated in the deposited layers.

Before discussing the classification of the growth modes in terms of thickness variation of chemical potential, we first derive the classical Bauer's criterion.

29.2.2

Bauer's Criterion for the Equilibrium Shape

The classification of the epitaxial growth modes was originally given by Bauer as a result of a thermodynamic analysis of the wetting of the substrate by the deposit film [17]. Here, we derive the same criterion following the atomistic approach to the equilibrium shape of the deposit crystal, first introduced by Stranski and Kaischew [16, 18, 19].

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Figure 29.2 (a) Representation of Kossel crystal; the most important sites an atom can occupy on the crystal surface are indicated: one-atom adsorbed on the crystal face, two-atom adsorbed at the step edge, three-atom in half-crystal (kink) position,

four-atom embedded into the step edge, and five-atom incorporated into the face. (b) ψ_1 , ψ_2 , and ψ_3 are the interaction energy between first, second, and third nearest neighbors, respectively.

The simplest atomistic model of a crystal was developed by Kossel [20] and consists of a simple cubic crystal in which the binding of atoms is assumed to be only determined by the number of neighbors. Despite its simplicity, this model provides a viable route to bridge the thermodynamic and atomic descriptions of crystal growth. In Kossel's model, atoms are represented as cubes with interaction energy ψ_1 between nearest neighbors (cubes sharing a common face) and ψ_2 between next-nearest neighbors (cubes sharing a common edge); longer-range interactions are much weaker and are omitted, for simplicity. (Figure 29.2).

The specific surface energy of a crystal face is evaluated from the energy necessary for detachment of an additional column of atoms from the same face. For the (100) surface, the value of the surface energy is then

$$\sigma_{100} = \frac{\psi_1 + 4\psi_2}{2a^2} \tag{29.3}$$

as one bond between first neighbors and four bonds between second neighbors should be broken. The interatomic distance *a* determines the area per atom, a^2 .

The atomistic approach of Stranski and Kaischew can be also used to find the equilibrium shape of a 3D crystal lying on a foreign substrate. Because at the equilibrium the probability of building up a new crystal plane should be equal to the probability of its dissolution, the energy per atom of disintegration of a crystal plane into single atoms is a measure of the equilibrium and must have one and the same value for all crystal planes belonging to the equilibrium shape. This equilibrium energy value is known as *mean separation work*.

Consider a Kossel crystal with n atoms in the horizontal edges and n' atoms in the vertical edges deposited on a foreign substrate with cubic structure as well (Figure 29.3). Following the steps of the disaggregation process schematized in Figure 29.4a, the mean separation work calculated for the top (100) face is

$$\varphi_{(100)} = \frac{1}{n^2} [n^2 \psi + 2n(n-1)\psi] = 3\psi - \frac{2\psi}{n}$$
(29.4)

where only first-neighbor bonds ($\psi_1 \equiv \psi$) have been considered. Note that only bonds between like atoms are broken in the disintegration of the upper base.



Figure 29.3 Kossel crystal with n atoms in the horizontal edges and n' atoms in the vertical edges deposited on a foreign substrate.



Figure 29.4 For the evaluation of the equilibrium shape of a crystal lying on a foreign substrate according to the atomistic approach of Stranski and Kaischew. n and n' denote the numbers of atoms in the horizontal and vertical edges, respectively. The different steps and the corresponding energy

costs for disintegration of (a) the upper crystal face and (b) of the side face are indicated: first, the crystal plane is detached from the crystal block; then the plane is disintegrated into atom rows and each row is disintegrated into single atoms.

On the other hand, it is found from Figure 29.4b that the energy needed for disintegration of the side (001) face is

$$\varphi_{(001)} = \frac{1}{n'n} [nn'\psi + n\psi' + n'(n-1)\psi + (n'-1)n\psi] = 3\psi - \frac{\psi - \psi'}{n'} - \frac{\psi}{n}$$
(29.5)

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Figure 29.5 For the determination of the specific energy of the interface between a deposit crystal (D) on a foreign substrate (S).

where ψ' is the energy to break a bond between unlike atoms. At the equilibrium, the mean separation works of the different faces have to be equal ($\varphi_{(100)} = \varphi_{(001)}$) and this condition determines the equilibrium shape ratio n'/n of the deposit crystal as

$$\frac{n'}{n} = \frac{\psi - \psi'}{\psi} \tag{29.6}$$

Taking n' = 0 as a condition for a 2D nucleus, it can be inferred from Equation 29.6 that the crystallization process proceeds with VW growth of 3D adatom clusters or islands when adatom–adatom interactions are stronger than those of the adatom with the surface (i.e., $\psi > \psi'$). The opposite case, in which the overlayer–substrate interaction exceeds the interaction between neighboring adatoms ($\psi \le \psi'$), leads to the 2D FM growth mode.

To recover the usual 3- σ Bauer's criterion, we have to reformulate Equation 29.6 in terms of surface energies. To this end, we examine the energy balance of the following process (Figure 29.5): (i) dissociation of a pair of substrate atoms (S) and a pair of deposit atoms (D) and (ii) formation of two pairs of S–D dimers. For the dissociation step (i), we expand the energies ψ_S and $\psi_D = \psi$, whereas we gain energy $-2\psi_{S-D} = -2\psi'$ during step (ii). The excess energy required to balance the above-mentioned process is $2\psi_i$

$$2\psi_{\rm i} = \psi_{\rm S} + \psi - 2\psi' \tag{29.7}$$

Using the definitions of the specific surface energy $\sigma_{\rm S} = \psi_{\rm S}/2a^2$ and $\sigma = \psi/2a^2$ for the substrate and the deposit crystal, respectively, we obtain

$$\sigma_{\rm i} = \sigma_{\rm S} - \sigma + \frac{\psi - \psi'}{a^2} \tag{29.8}$$

where the specific interfacial energy $\sigma_i = \psi_i/a^2$ is defined as the excess energy of the boundary per unit area. Combining Equations 29.6 and 29.8, we deduce the Bauer's criterion from the condition for equilibrium shape of a 3D cubic nucleus on a foreign substrate

$$\frac{n'}{n} = \frac{\psi - \psi'}{\psi} = \frac{\sigma + \sigma_{\rm i} - \sigma_{\rm S}}{2\sigma} = \frac{\Delta\sigma}{2\sigma}$$
(29.9)

As follows from the previous equation, the so-called *adhesion parameter* $\Phi = 1 - \psi'/\psi$ [21] is equivalent to the Bauer's surface energy change $\Delta\sigma$ and accounts for the wetting of the substrate by the overgrowth. The limiting cases of VW and FM growth occur, respectively, for $0 < \Phi < 1$ and $\Phi \leq 0$.

In case a lattice misfit f between substrate and deposit crystal is present, an additional contribution due to strain and, eventually, dislocation energy is introduced in the interfacial energy, which becomes

$$\sigma_{i}^{*} = \sigma_{i} + \Xi_{el}(\varepsilon) + \Xi_{disl}(f - \varepsilon)$$
(29.10)

where the strain energy per unit area $\Xi_{\rm el}$ and the misfit dislocation energy $\Xi_{\rm disl}$ per unit area depend on the homogeneous strain ε and the dislocation density $f - \varepsilon$, respectively. A perceptible misfit, $\sigma_{\rm i}^*$ is indeed responsible for the transition from layer-by-layer growth to 3D growth in the SK mode. The latter mechanism is therefore characterized by the conditions $\Phi < 0, f \neq 0$.

29.2.3 Thickness Variation of Chemical Potential and Growth Modes

The position of an atom on a crystal surface determines how strongly the atom itself is bounded to the crystal. Consider as an example the cubic face of a Kossel crystal depicted in Figure 29.2. We recognize five different atomic sites: (i) atoms incorporated into the outermost crystal plane or (ii) embedded into the step edge; (iii) atoms in kink position or adsorbed either (iv) at the step or (v) on the crystal face. For all the positions except site (iii), atoms have a different number of saturated and unsaturated bonds, and detachment from these sites results in a change in the surface energy. For kink sites, however, detachment has exactly the same energetic balance as attachment has, and therefore the two events occur with the same probability. It follows that the equilibrium vapor pressure P_{∞} and chemical potential μ_{∞} of a bulk crystal is determined by the work of separation from kink sites $\varphi_{1/2}$ [19–22]:

$$\mu_{\infty} = \mu_0 + kT \ln P_{\infty} = -\varphi_{1/2} + kT \ln \left[\frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{h^3}\right]$$
(29.11)

where *m* is the atomic mass, *h* the Planck constant, and $\mu_0 = \mu_{\infty}(T = 0)$. As the work $\varphi_{1/2}$ is always equal to the energy required to break half of the bonds of an atom situated in the bulk of the crystal, the kink site is also known as the *half-crystal position*.

From Figure 29.2, it can be easily seen that to detach an atom from the half-crystal site of a bulk Kossel crystal, if only first-neighbor bonds are considered, three bonds have to be broken: two lateral bonds with half-crystal plane and half-crystal row and one normal bond with the underlying half-crystal block. Thus, $\varphi_{1/2} = 3\psi$. Consider a monolayer on the surface of a foreign crystal, and work of separation from the half-crystal position $\varphi'_{1/2}$ now reads

$$\varphi'_{1/2} = 2\psi + \psi' = \varphi_{1/2} - (\psi - \psi')$$
(29.12)

where the normal bonding with the foreign substrate atoms has been taken into account. Bearing in mind Equation 29.11, we find that the chemical potential of the



Figure 29.6 Chemical potential of (a) a bulk deposit and (b) of a thin epilayer.

overgrowth layer μ is related to that of the bulk deposit crystal μ_{∞} (Figure 29.6) by

$$\mu = -\varphi'_{1/2} + kT \ln\left[\frac{(2\pi m)^{\frac{3}{2}}(kT)^{\frac{5}{2}}}{h^3}\right] = \mu_{\infty} + (\psi - \psi')$$
(29.13)

Combining Equations 29.8 and 29.13, we can write the chemical potential of the adsorbed monolayer in terms of the change of the surface energy connected with its deposition

$$\mu = \mu_{\infty} + (\psi - \psi') = \mu_{\infty} + a^{2}(\sigma_{i} + \sigma - \sigma_{S})$$
(29.14)

In the above-mentioned equation, the interatomic energies ψ and ψ' have, respectively, the meaning of the energy of desorption of an atom from the same crystal φ_d and from a foreign substrate φ'_d .

As evident from Equation 29.14, the chemical potential of the first deposited monolayer differs from that of the bulk deposit crystal. This is partly due to the modified atomic interaction across the interface (i.e., $\psi' \neq \psi$ or equivalently $\varphi'_{d} \neq \varphi_{d}$). On the other hand, the lattice misfit leads to the appearance of homogeneous strain and misfit dislocations. Obviously, the presence of the substrate will affect differently the atoms in the first, second, and third layers, and so on. Combining Equations 29.10 and 29.14, we make explicit the dependence on the overlayer thickness and obtain the generalized expression for the chemical potential of the *n*th monolayer deposited on the foreign substrate in the presence of lattice misfit

$$\mu(n) = \mu_{\infty} + [\varphi_{d} - \varphi_{d}'(n) + \xi_{el}(n) + \xi_{disl}(n)] = \mu_{\infty} + a^{2}(\sigma_{i}^{*}(n) + \sigma - \sigma_{s})$$
(29.15)

where $\xi_{\rm el} = a^2 \Xi_{\rm el}$ and $\xi_{\rm disl} = a^2 \Xi_{\rm disl}$ are the energies per atom of the homogeneous strain and misfit dislocations. By inspecting Equation 29.15, it is clear that the Bauer's criterion of the growth mode in terms of $\Delta\sigma$ can be reformulated on the basis of the variation of the chemical potential with the film thickness. That is, the condition $\Delta\sigma < 0$ for FM growth is equivalent to $\Delta\mu \equiv \mu(n) - \mu_{\infty} < 0$, whereas VW islanding will occur for $\Delta\mu > 0$ (Figure 29.7). In the case of SK growth, a planar film is deposited as long as $\mu(n) < \mu_{\infty}$; at a certain critical coverage n_c , the chemical potential of the 2D film becomes higher than that of the bulk deposit crystal and 3D islands are formed (Figure 29.7).



Number of monolayers

Figure 29.7 Schematic representation of the dependence of the chemical potential on the film thickness for Volmer–Weber (VW), Stranki–Krastanov (SK), and Frank–van der Merwe (FM) growth. Adapted from [21].

29.2.4 Generalized Thermodynamic Criterion for the Mechanism of Growth

In the previous section, we derived the thermodynamic condition for occurrence of planar growth and clustering by making a strong use of specialized arguments of crystal growth theory. Here, following the seminal work of Peierls [13], we show that the same results can be inferred directly from a very general discussion of the possible forms of the free energy of the film as a function of thickness.

Let G(n) be the Gibbs free energy per unit area of a uniform adsorbed layer containing *n* atoms per unit area. What we know for sure about the shape of G(n) is that the function decreases monotonically with *n*, as the chemical potential $\mu = \partial G/\partial n$ must be negative. In Figure 29.8, the simplest possible shape of G(n) satisfying the previous condition appears as a continuous line. The value of *G* for



Figure 29.8 Schematic dependence of the Gibbs free energy per unit area of a uniform film versus thickness n in case of a positive curvature from the very beginning of adsorption (layer-by layer growth). The dashed-dotted line is the asymptote to large n, and the dashed line is the tangent at an arbitrary n. Adapted from Peierls [13].

n = 0, that is, the intercept with the *G*-axis, is obviously the free surface energy, $\sigma_{S,0}$, of the interface substrate-vacuum. On the other hand, because at large *n* the system consists of a substrate and a thick adsorbate, the asymptote (dashed-dotted line) gives the free energy of the bulk adsorbate. For large *n*, there will be an interface separating the adsorbate from the substrate and another one between the adsorbate and the vapor. Following the asymptote back to n = 0, we make the adsorbate thinner, leaving the energies of the phase boundaries only. Therefore, α_{∞} (Figure 29.8) is given by

$$\alpha_{\infty} = \sigma + \sigma_{\rm i} \tag{29.16}$$

where σ_i and σ are the free energies of the substrate-adsorbate and adsorbate-vapor interface, respectively.

The tangent at an arbitrary *n* (dashed line) has an intercept with the *G*-axis, which we define $\alpha(n)$. Evidently

$$\alpha(n) = G(n) - n \frac{\mathrm{d}G}{\mathrm{d}n} \tag{29.17}$$

and differentiating the above-mentioned equation one obtains

$$\frac{\mathrm{d}\alpha(n)}{\mathrm{d}n} = -n\frac{\mathrm{d}^2G}{\mathrm{d}n^2} = -n\frac{\mathrm{d}\mu}{\mathrm{d}n}$$
(29.18)

or, equivalently,

$$d\alpha(n) = -nd\mu \tag{29.19}$$

This is identical with the Gibbs adsorption isotherm

$$\mathrm{d}\sigma_{\mathrm{s}}(n) = -n\mathrm{d}\mu\tag{29.20}$$

which correlates the change $d\sigma_s(n)$ in the surface energy of the substrate with the amount *n* per unit area of an adsorbate of chemical potential μ . Clearly, the interfacial tension between the solid and the vapor is affected by adsorption; this results in a reduction in σ_s of an amount equal to the so-called spreading pressure ϕ of the film [23]

$$\phi = -\mathrm{d}\sigma_{\mathrm{s}}(n) \tag{29.21}$$

Bearing in mind Equation 29.21, we combine Equations 29.19 and 29.20 and obtain, after integration,

$$\alpha(n) = -\phi + C \tag{29.22}$$

where *C* is an integration constant. For n = 0, ϕ vanishes, whereas it is evident from Figure 29.8 that α is $\sigma_{S,0}$. Then, $C = \sigma_{S,0}$ and

$$\alpha(n) = -\phi + \sigma_{S,0} = \sigma_S(n) \tag{29.23}$$

Subtracting Equation 29.23 from Equation 29.16, we link the shape of the free energy with the Bauer's criterion in terms of surface energies

$$\alpha_{\infty} - \alpha(n) = \sigma + \sigma_{\rm i} - \sigma_{\rm S} \tag{29.24}$$



Figure 29.9 Schematic dependence of the Gibbs free energy per unit area of a uniform film versus thickness *n* in case of a negative curvature from the very beginning of adsorption (3D islanding). The dashed-dotted line is the asymptote to large *n*. Adapted from Peierls [13].

If *G*(*n*) tends to the asymptote from the above, as in the case illustrated in Figure 29.8, evidently $\alpha_{\infty} - \alpha(n) < 0$; this means the condition for complete wetting $\Delta \sigma < 0$ is satisfied for all *n*. We also notice that for the shape of *G*(*n*) shown in Figure 29.8 the curvature is everywhere positive. Thus, complete wetting occurs when $d^2G/dn^2 > 0$ or, in other words, when $d\mu/dn > 0$. As every next monolayer has a higher chemical potential, the completion of the first monolayer before the start of the second one, of the second before the start of the third, and so on, is thermodynamically favored and layer-by-layer growth is therefore expected. In fact, the chemical potential $\mu = dG/dn$ of the planar film is everywhere lower than that of the bulk adsorbate, μ_{∞} , which is the slope of the asymptote.

In the opposite situation, when G(n) has a negative curvature all the way (Figure 29.9), $\alpha_{\infty} > \alpha(n)$ for all *n* and, thus, $\Delta \sigma > 0$. As the latter conditions imply that $d\mu/dn < 0$, the formation of a second monolayer before the completion of the first one is thermodynamically favored, leading to 3D islanding. As expected, in this case the chemical potential of the bulk adsorbate μ_{∞} (i.e., the slope of the asymptote) is lower than μ for all *n*.

The case of SK growth corresponds to a curve G(n) with an inflection point (Figure 29.10). In this case, there exists a coverage n_c for which the tangent is parallel to the asymptote, that is, the film has the same chemical potential of the bulk adsorbate μ_{∞} . Between 0 and n_c , a planar film is still stable and the chemical potential μ rises with n to reach the bulk value at n_c . The amount of adsorbate at $n = n_c$, which wets completely the substrate is known as the *wetting layer*. For $n > n_c$, the uniform layer is unstable, and clusters with bulk properties are thus formed.

It can be noticed that differentiation of the G(n) curves in Figure 29.8, Figure 29.9, Figure 29.10 gives the three $\mu(n)$ curves shown in Figure 29.7. It follows that the three classes defined by Peierls and Dash [13, 23] on the basis of thickness dependence of the free energy represent the mechanisms of growth of thin epitaxial films.

29.3 Stability of the Quantum Dot Morphology

In molecular beam epitaxy (MBE), films are grown from gaseous precursors. The substrate acts as a seed crystal providing a template for positioning the first



Figure 29.10 Schematic dependence of the Gibbs free energy per unit area of a uniform film versus thickness n in case an inflection point is present (SK growth). The dashed-dotted line is the asymptote to large n. At

the coverage n_c the tangent to G(n) is parallel to the asymptote and has a slope equal to the bulk chemical potential μ_{∞} . Adapted from Peierls [13].

impinging atoms of the film, and each atomic layer has the same function for the next layer. As illustrated in Section 29.2.1, in the heteroepitaxy of a material *A* on a substrate *B*, the growth morphology is mainly determined by the surface energies of the overlayer, of the substrate, and of the interface. The SK growth occurs when there is an initial wetting of the substrate but, with increasing overlayer thickness, surface energies are changed by surface stress or by interface mixing and/or segregation, so that at a critical thickness of *A* the initial wetting condition does not hold anymore and islands start forming from then on. As it will be shown in this section, the strain inherently introduced in lattice mismatched systems is at the origin of 3D islanding.

Strain in heteroepitaxy has a twofold origin: (i) the difference in the lattice parameters and (ii) the difference in the thermal expansion coefficient between the epilayer and the substrate. Although, in most cases, both parameters have different values in the epitaxial layer and in the substrate, the lattice parameter mismatch is generally the more significant of these two parameters. For example, the lattice constants of Si and Ge at room temperature are $a_{\rm Si} = 5.432$ Å and $a_{\rm Ge} = 5.658$ Å. Thus, the lattice mismatch in the Ge/Si system at room temperature is approximately 4×10^{-2} . On the other hand, the linear thermal expansion coefficient of Si and Ge are 2.7×10^{-6} K⁻¹ and 5.9×10^{-6} K⁻¹, respectively [24]. This produces a difference in thermal expansion coefficient of Si and Ge of order 3.2×10^{-6} and a strain of order (3.2×10^{-6}) δT for a temperature change of δT . Therefore, even considering a temperature incursion of 1273 K, which corresponds



Figure 29.11 Schematics of an epitaxial layer pseudomorphically grown on a foreign substrate. As the intrinsic lattice parameter of the epilayer is larger than that of the substrate (panel (a)), the unit cell of the film is tetragonally distorted (panel (b)).

to the maximum practical growth temperature on the Ge/Si system, thermal strains are one order of magnitude less than lattice mismatch strains.

When the growth of the overlayer is *pseudomorphic* or *coherent*, the heteroepitaxial layer does not keep its own lattice constant a_e but is tetragonally distorted to the substrate lattice parameter a_s (Figure 29.11). The lattice mismatch f between the substrate and the epilayer is defined as $f = (a_e - a_s)/a_e$. If the lattice parameter difference is accommodated entirely elastically (without the formation of misfit dislocations), and ignoring the effects of differential thermal expansion coefficients, the elastic strain of the epilayer in the plane of the interface is given by

$$\varepsilon_{//} = 2 \frac{(a_{\rm s} - a_{\rm e})}{(a_{\rm e} + a_{\rm s})} \approx \frac{(a_{\rm s} - a_{\rm e})}{a_{\rm e}} = -f$$
 (29.25)

For $a_e > a_s$, as in the case of Ge/Si, the strain in the epitaxial layer is compressive and $\varepsilon_{//}$ is negative; for $a_e < a_s$, the film is stretched and the in-plane strain is tensile ($\varepsilon_{//} > 0$). Owing to the biaxial in-plane distortion, the epitaxial layer relaxes along the interface normal and produces an out-of-plane strain component

$$\varepsilon_{\perp} = 2 \frac{\nu}{(1-\nu)} f \tag{29.26}$$

where v is the Poisson ratio of the epilayer material. This means that biaxial compression within the pseudomorphic Ge layers grown on Si induces an outward distortion in the growth direction. For $v_{Ge} = 0.273$, one finds that the lattice constant of a Ge film along the interface normal is about 3% larger.

The elastic strain energy per unit area (Equation 29.10) stored in the epitaxial film is

$$\Xi_{\rm el} = \frac{E}{(1-\nu)} \varepsilon_{//}^2 d \tag{29.27}$$

where *E* is the Young's modulus and *d* the film thickness. For a Ge/Si film, we have E = 103 GPa [24] and therefore an elastic energy density $\rho_{2D} = E\epsilon_{//}^2 (1 - \nu)$ of 1.41 meV Å⁻³. For an epilayer thickness of 50 Å, this produces a surface strain energy of ~ 70 meV Å⁻² comparable to the magnitude of surface energies. As the



Figure 29.12 For the evaluation of the free-energy gain of 3D islanding with respect to a flat film. α is the contact angle of the 3D pyramid of height *h* and lateral edge *L*.

elastic energy increases linearly with layer thickness (Equation 29.27), it possibly drives the 2D-to-3D growth transition.

The critical thickness d_c at which islanding takes place can be determined by examining the free-energy balance of a planar epilayer film of volume *V* with respect to a configuration in which an island of the same volume is formed on a very thin 2D WL [25–27] (Figure 29.12). The total free energy of the 2D configuration (Figure 29.12a) reads

$$F_{\rm 2D} = \frac{E}{(1-\nu)} \varepsilon_{//}^2 V + (\sigma + \sigma_i) S_{\rm film}$$
(29.28)

where the first term gives the elastic strain energy and the second one gives the surface energy of the film σ of area S_{film} and the island–substrate interface energy σ_i . For the configuration of Figure 29.12b, the total free energy is instead

$$F_{\rm 3D} = R \frac{E}{(1-\nu)} \varepsilon_{//}^2 V + (\sigma + \sigma_{\rm i}) S_{\rm film} + \gamma S - \sigma B$$
(29.29)

where γ is the specific free energy of the island facets of area *S* and *B* is the base area. Note that the formation of a 3D island enables the elastic relaxation of strain, reducing the elastic energy term of a factor *R* < 1 with respect to the planar film. It follows that the trade-off between the 3D and the 2D configurations becomes

$$\Delta F = (R-1)\frac{E}{(1-\nu)}\varepsilon_{//}^2 V + \gamma S - \sigma B$$
(29.30)

Obviously, both the surface energy cost and the strain energy relaxation due to island formation inherently depend on the island shape. Incidentally, we note that edge energies of the island, scaling as $V^{1/3}$, have been omitted in Equations 29.29 and 29.30. Considering a regular square-based pyramid with facet inclination α , we derive the analytical expression of the base and lateral surface areas in terms of the island volume and assume, for concreteness, $\gamma = \sigma$, obtaining

$$\Delta F = (R-1)\frac{E}{(1-\nu)}\varepsilon_{//}^2 V + \gamma \left(\frac{6}{\tan\alpha}\right)^{\frac{4}{3}}(\sec\alpha - 1)V^{\frac{2}{3}}$$
(29.31)



Figure 29.13 Critical thickness d_c for 3D islanding as a function of the island contact angle α .

3D-to-2D islanding occurs when F_{2D} becomes larger than F_{3D} , namely, at the critical film volume V_c for which $\Delta F = 0$. Thus, the critical thickness at which islanding takes place can be estimated as

$$d_{\rm c} = V_{\rm c}^{\frac{1}{3}} = \frac{\Delta F_{\rm s}(1-\nu)}{(1-R)E\varepsilon_{//}^2}$$
(29.32)

where we write $\Delta F_s = \gamma (6/\tan \alpha)^{\frac{2}{3}} (\sec \alpha - 1)$ for compactness. For very shallow islands, the elastic problem has an approximate solution $(1 - R) \propto \tan \alpha$ [25–28]. The resulting behavior of d_c as a function of the contact angle of the island facets is shown in Figure 29.13. Despite being highly simplified, the plot shows that the evolutionary path for the 2D-to-3D transition is one for which the contact angle increases continuously from planar to a 3D morphology [29, 30]. This is because the surface free-energy term ΔF_s , causing the formation of a 3D morphology to be an activated process, scales with the sidewall angle of the islands. Less new surface is created when the morphology is shallower, and hence the activation energy is also lower.

This *continuous* islanding process is experimentally observed in Ge/Si heteroepitaxy and occurs between 3.2 and 3.8 monolayers (ML) of Ge (1 ML = 1.4 Å) [31-33]. Figure 29.14 shows the onset of 3D islanding of Ge on the Si(001) surface imaged in real time during the growth using scanning tunneling microscopy (STM) [33]. It can be seen that the initial step of the 3D transition takes place via the formation of shallow mounds with a height-to-base ratio ranging between 0.015 and 0.03, which become progressively larger and steeper and finally evolving in complete square-base pyramids bounded by {105} facets.

In order to obtain more quantitative information, one has to abandon the mathematical simplicity of isotropic elasticity. In fact, silicon and germanium are highly anisotropic materials, with elastic behavior that depends on the crystal





Figure 29.14 Real-time STM experiment studying the growth of Ge pyramids on the Si(001) surface. (a) Evolution of the profile of the pyramid versus coverage. (b–i) STM images $(250 \times 80 \times 3) \text{ nm}^3$ extracted from the movie of Ge deposition at 500°C for increasing Ge coverage.

orientation. For example, the possible values of the Young's modulus for Si range from 130 to 188 GPa [34] and, hence, the use of an average elastic constant is a significant approximation producing errors of an order of 10–20%. We shall therefore make use of complete anisotropic description in the subsequent analysis.

We recall that the fundamental law of linear elasticity – that is, Hooke's law – describes the relationship between stress σ and strain e in terms of stiffness **C**

$$\sigma = C \varepsilon \tag{29.33}$$

For isotropic uniaxial crystals, stiffness **C** can be represented by a single value of Young's modulus *E*. In an anisotropic material, a fourth rank tensor with $3^4 = 81$ terms is required to relate the second rank tensors of stress and strain. In this case, Hooke's law is written as

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \tag{29.34}$$

Note that all indices span between 1 and 3 and that the sum over repeated indices is understood. In cubic semiconductors such as Si and Ge, the complex stiffness tensor is described by three independent components, the values of which are summarized in Table 29.1.

 Table 29.1
 Lattice and elastic constants of Ge and Si.

Element	Si	Ge
Lattice parameter: <i>a</i> (Å)	5.432	5.658
Elastic moduli: C ₁₁ (GPa)	160.2	121.6
C ₁₂ (GPa)	62.1	46.5
C ₄₄ (GPa)	76.2	64.3

For the (001) crystal plane, the Poisson ratio and the Young's modulus in terms of the anisotropic elastic constants become

$$v_{001} = \frac{C_{12}}{(C_{11} + C_{12})}; \qquad \qquad E_{001} = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})}$$
(29.35)

and the elastic strain energy per unit area (Equation 29.27) of an anisotropic planar epitaxial film is

$$\Xi_{\rm el} = \left[C_{11} + C_{12} - 2\frac{C_{12}^2}{C_{11}} \right] \varepsilon_{//}^2 d \tag{29.36}$$

The determination of the elastic relaxation for realistic 3D island's shapes is, however, a challenging task. Several approaches have been applied to the computation of elastic fields in semiconductor QDs. As already mentioned, continuum models giving analytical solutions have the advantage of giving fast, semiquantitative estimates. Most of them are based on the usage of Green's functions: starting from the Green function of a point-like inclusion of the deposit crystal on a semi-infinite substrate [35], the elastic field due to a macroscopic island is obtained integrating this function over the island volume. For example, the estimate of *R* giving the qualitative behavior of d_c in Figure 29.13 is based on a method, commonly known as *flat-island approximation*, developed in this framework [26], [36]. Generally, the method fails in determining the elastic fields in steep islands, even if an improvement has been recently proposed, which has shown to yield consistent estimates also for this case [37]. The critical drawback for analytical solutions to the elastic problem is that they can be computed for simple island shapes only.

To handle the complexity of realistic 3D geometry, one has to employ the computational power of numeric simulations. Two approaches are particularly suited for determining key phenomena associated with strain energy relaxation in QD structures: molecular dynamics (MD) and finite element (FE) methods. In MD, strain distribution is obtained starting from the interactions and the displacements of single atoms in the system. Being atomistic, MD simulations have the advantage of taking into account atomic-scale features, such as surface reconstructions, or inhomogeneous alloying [38–44]. On the other hand, MD calculations are computationally very demanding when treating systems, such as semiconductor QDs, which consist of a few million atoms. For this scale, finite

element (FE) simulations have been shown to be robust and reliable by direct comparison with atomistic calculations [45], being, however, much more easily accessible [46–48].

The basic premise of an FE calculation is that the elastic body can be approximated by an assemblage of discrete elements (typically a tetrahedron for 3D problems). The set of elements, together with their vertices (*nodes*), constitute the finite *mesh*. Generally, the distribution of the mesh element is not uniform throughout the space, but is made finer in regions where the elastic energy is expected to be higher – that is, inside the island. The core idea is that the nodal values of any field variable $f(\mathbf{r})$ and the interpolation functions for the elements completely define the behavior of the field variable within the elements.

Consider the model depicted in Figure 29.15, that is, a deposit crystal in the shape of a pyramid on a substrate having different lattice parameters. In particular, hereafter we discuss the case of a compressive deposit crystal. The initial strain condition is set by the lattice mismatch *f*: before relaxation, the deposit is compressively strained to the substrate lattice parameter in the three perpendicular directions (in plane *x* and *y*, and out-of-plane *z*) and the initial condition thus reads $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = -f$, where ε_{xx} , ε_{yy} , and ε_{zz} represent the three diagonal component of the strain tensor. Indeed, lattice mismatch is at the origin of the stress field in the heteroepitaxial structure. In the framework of continuum elasticity, a



Figure 29.15 Geometric model of a Ge pyramid on a Si(001) substrate used in FE simulations.

crucial problem is how to mimic the lattice mismatch [49]. As it will be shown in the following, the misfit strain experienced by the island can be conveniently treated following the Eshelby formalism for inclusions [50]. An *inclusion* is a region completely embedded in a surrounding medium (*matrix*), which undergoes a permanent deformation. If taken away from the medium, the inclusion would experience a deformation to restore the zero-stress condition, assuming a uniform strain ε_{ij}^* called *eigenstrain*. Therefore, the eigenstrain is defined as the value of the strain field at which the stress field is zero by the following equation

$$\sigma_{ij} = C_{ijkl}(\varepsilon_{ij} - \varepsilon_{ij}^*) \tag{29.37}$$

In our epitaxial system, the island acts as a stressor, leading to a condition of stress due to the lattice mismatch. According to the eigenstrain principle, if we were able to take the compressed island away from the substrate, it would undergo an elastic dilation to recover its own lattice parameter. As a consequence, the eigenstrain is simply

$$\varepsilon_{ij}^* = f \,\delta_{ij} \tag{29.38}$$

where δ_{ij} is the Kronecker delta. In point of fact, the island is not able to reach the state of eigenstrain – that is, the condition of zero stress – but both the substrate and the island deform in order to minimize the elastic energy: solving the elastic problem of a heteroepitaxial island involves finding the displacement field due to the condition of eigenstrain in the entire space which is, as a matter of fact, the Eshelby's problem of inclusion. Thus, the final elastic-energy distribution can be obtained by allowing the system to relax, as far as the elastic equilibrium is reached. At the equilibrium, the sum of forces inside the elastic body has to balance the external force T_i acting on it; thus, the equilibrium equation can be written as

$$-\frac{\partial}{\partial x_i}\sigma_{ij}(\mathbf{u}) = T_i \tag{29.39}$$

where **u** is the displacement field. In our case, there are no external forces, as the island itself is at the origin of the stress in the system; so, $T_i = 0$. With reference to Figure 29.15, two types of boundary conditions are applied. The Dirichlet condition $u_i = 0$ is imposed on the bottom of the simulation box, whereas the other boundaries are free surfaces at which the null-stress condition $\sigma \cdot \mathbf{n} = 0$ holds (**n** is the normal to any free surface). The elastic problem described by Equation 29.39 is solved self-consistently using the constitutive stress–strain relations 29.37 and 29.38 which, for a cubic symmetry, have the form

$$\sigma_{ii} = (C_{11} - C_{12})\varepsilon_{ii} + C_{12}f$$

$$\sigma_{ij} = C_{44} \varepsilon_{ij} \quad (i \neq j)$$
(29.40)

Once the initial strain condition is assigned, the FE solver determines by an iterative procedure the displacement field \boldsymbol{u} minimizing the elastic energy (per unit volume) of the system $\rho = \frac{1}{2} \sum_{klmn} C_{klmn} \varepsilon_{kl} \varepsilon_{mn}$ which, for a structure with cubic

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structure, reduces to

$$\rho = \frac{C_{11}}{2} (\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2) + 2C_{44} (\varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{xz}^2) + 2C_{12} (\varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{xx} \varepsilon_{zz} + \varepsilon_{yy} \varepsilon_{zz})$$
(29.41)

After minimization, the total elastic energy of the system is evaluated by integrating the local energy density over the island and the substrate volumes

$$\rho_{3\mathrm{D}} V = \left(\int_{\mathrm{isl}} \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} + \int_{\mathrm{sub}} \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} \right)$$
(29.42)

So far, the thin WL under the island has not been taken into account. Introducing a very thin layer in FE calculations requires a high number of mesh elements, which increases the computational effort. Moreover, as the thickness of the WL is fixed (e.g., \sim 3 ML for Ge/Si) independently of the island size, its weight over the whole elastic body depends on the island volume. Thus, FE simulation including the WL is not fully self-similar. A relevant question to be addressed is the extent to which neglecting the WL affects the simulations. A rough estimate of the weight of WL is inferred by evaluating the total energy E_{sub} stored in the substrate (i.e., the second integral in Equation 29.42) with and without this thin planar epilayer.

In Figure 29.16, the normalized change of E_{sub} has been calculated for Ge/Si pyramids having the same volume but different facet inclination. It can be seen that the WL plays a role in the elastic relaxation of the system only for very shallow island morphology. Steeper islands, in fact, exert an elastic loading deeper in the substrate and as such the presence of the WL becomes, in their case, negligible.

FE simulations can be successfully used to evaluate the relaxation factor *R* appearing in Equation 29.31 for 3D island shapes within anisotropic elasticity.



Figure 29.16 Relative weight of WL in FE simulations as a function of the facet inclination of Ge pyramid. E_{sub}^{WL} is the elastic energy stored in the substrate including the WL, whereas E_{sub} is the same term neglecting the presence of the WL.



Figure 29.17 Relaxation factor as a function of the aspect ratio of Ge pyramids. Data obtained by FE calculations (squares) are fitted by an exponential decay curve (continuous line).



Figure 29.18 Cross-sectional maps of the ε_{xx} strain component for Ge islands of aspect ratio (a) r = 0.1 and (b) r = 0.7.

For a direct comparison with experimental data, the island geometry is usually expressed in terms of the height to-square-root of the base ratio or *aspect ratio r*. For square-based pyramids, *r* is simply $\tan \alpha/2$. In Figure 29.17, we report the aspect-ratio dependence of the relaxation factor for pure Ge islands grown on the Si(001) surface. It can be clearly seen that *R* decreases monotonically as the facet inclination gets higher, thus indicating that steeper structures provide a better elastic relaxation. The underlying reason can be found by carefully analyzing the strain distribution after elastic relaxation for different island shapes (Figure 29.18). The maps are vertical cross sections of the ε_{xx} strain tensor component inside the islands. A common feature is the highly nonuniform strain field both in the island and in the substrate. As opposed to the homogeneous case of a planar film (Equations 29.25 and 29.26), in 3D structures elastic energy relief is based on strain redistribution within the island and on strain propagation inside the substrate. Directly under the island, the Si lattice is expanded and the tensile dilation induces

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a consequent compression immediately outside the island edges. Inside the island, the compressive strain field decreases, moving from the substrate toward the island top, where the elastic relaxation is higher. By comparing the two strain maps, it is clear that the steeper the island, the more effective is the relaxation of misfit strain. The functional dependence of the relaxation factor is not restricted to the pyramid case but it holds also for other geometrical shapes [51]. It is therefore tempting to find an analytical form to describe the behavior of *R* as a function of the aspect ratio. A simple exponential form [52] $R(r) = e^{-kr}$ with k = 1.839 is suitable to fit FE data except at high values of *r* (Figure 29.17). Clearly, steep islands provide better elastic relaxation, but, on the other hand, they exert an elastic load that penetrates more deeply into the substrate, as shown in Figure 29.18. The effect of substrate loading is correctly taken into account in (Equation 29.42), whereas it is neglected by using a single-exponential decay fitting function. To compensate for this bias, one could add a positive exponential e^{k_2r} factor to R(r) [49].

Using a single exponential for R(r), the total energy difference between the island and planar configurations (Equation 29.31), written in terms of the aspect ratio r, turns into a fully analytical form

$$\Delta F(r,V) = (e^{-kr} - 1)\rho_{WL}V + \gamma \left(\frac{3}{r}\right)^{\frac{2}{3}} \left(\sqrt{4r^2 + 1} - 1\right) V^{\frac{2}{3}}$$
(29.43)

where $\rho_{WL} = \Xi_{el}/d$. This provides a scaling expression for the energy balance driving the morphological evolution of islands with volume, which is useful for comparing the relative thermodynamic stability of different island shapes [52].

For a given volume, the equilibrium aspect ratio corresponds to the minimum of $\Delta F(r)$; therefore, the shape evolution with volume is found by setting $\frac{\partial \Delta F(r,V)}{\partial r} = 0$,



Figure 29.19 For the determination of the equilibrium island shape. Relaxation factor of the equilibrium island shape at increasing volume according to Equation 29.44.



Figure 29.20 Thermodynamically favored island's aspect ratio as a function of volume. The squares correspond to the solution of Equation 29.44 for different volumes.

giving

$$e^{-kr} = \frac{2}{3^{\frac{1}{3}}k} \left(\frac{\gamma}{\rho_{\rm WL}}\right) \left[\frac{2r^2 - 1 + \sqrt{4r^2 + 1}}{r^{\frac{5}{3}}\sqrt{4r^2 + 1}}\right] \frac{1}{V^{\frac{1}{3}}}$$
(29.44)

and solving Equation 29.44 for different volumes. As shown in Figure 29.19, the solution is straightforwardly obtained graphically and the aspect ratio as a function of the island's volume is illustrated in Figure 29.20. The general trend, that is, the increase in aspect ratio with island volume, is expected because, in the small-volume limit, the surface cost of islanding is dominant and shallow islands are energetically favored. As the volume grows, the volume term becomes increasingly important and, thus, the better elastic relaxation, provided by steeper morphologies, counterbalances the larger exposed surface.

What one learns from the above-mentioned simple model is that thermodynamics drives the morphological evolution of strained epitaxial nanostructures, dictating the progressive increase of aspect ratio with increasing island volume. This finding matches the experiment for a variety of semiconductor epitaxial systems [10].

Figure 29.21 shows experimental values of the aspect ratio as a function of volume for Ge islands grown on the Si(001) surface at 600 °C. As evident, the larger the island, the steeper is the island's facet inclination. By carefully inspecting the experimental plot, it can be seen that sudden slope changes at characteristic island volumes are superimposed on the monotonic increase of the *r* curve. These features correspond to distinct morphological transitions in the island's shape. In our oversimplified picture, we have assumed pyramid shapes only, but, actually, the overall geometry of islands also evolves as the Ge growth proceeds. This is apparent in Figure 29.22, where the principal islands' morphologies observed in Ge/Si(001) are shown. As already pointed out, at the onset of 3D islanding, very shallow mounds, referred to as *prepyramids* [31–33], are formed (Figure 29.22a). They have



Figure 29.21 Experimental evolution of island's aspect ratio with volume for Ge islands grown on Si(001). Arrows point to the discontinuities that indicate a shape change in the islands.

a low aspect ratio, ~0.04, and are nonfaceted. We remark that faceting is highlighted by applying an image-analysis tool known as *facet plot (FP)* to STM images [53]. It consists of a 2D histogram displaying the component of the surface gradient on the horizontal and vertical axes: faceting thus produces well-defined spots in the FP. The diffuse halo in Figure 29.22b therefore indicates that prepyramids do not contain distinct facets. Nonfaceted islands evolve into square-based pyramids (Figure 29.22c) when Ge growth continues [32]. As shown in panel (d), pyramids are bounded by four {105} facets, forming an angle of ~11° with the (001) plane (r = 0.1).

Faceting denotes anisotropic surface energy and it is therefore inconsistent with the assumption $\gamma = \sigma$ in Equation 29.31. In particular, the distinguishing features of the Ge(105) surface reconstruction [40, 54–56] makes the inclusion of surface energy anisotropy absolutely essential to match quantitatively the experimental results. The Ge(105) surface is a well-documented case of rebonded-step (RS) reconstruction stable surface. In the RS structure, the surface is partitioned into nanoscale {001} facets by nonrebonded S_A steps and rebonded S_B steps [55]. As a result, the uppermost dimers in the (2 × 1) unit cell form the characteristic array of U-shaped structures, organized into zigzag rows orthogonal to the [010] direction, which are observed in high-resolution filled-state STM images (Figure 29.23). Such a structure is highly stabilized under compressive strain and, therefore, the (105) surface energy results to be severely lowered in the Ge/Si heteroepitaxy. In order to include this effect in the total free-energy gain of islanding (Equation 29.30), a



Figure 29.22 STM images showing the principal islands' morphologies observed in Ge/Si(001) epitaxy: (a) prepyramids; (c) pyramids; (e) domes; and (g) barns. Panels (b), (d), (f), and (h) show the corresponding FPs.



Figure 29.23 STM image showing the RS reconstruction of the {105} facets of Ge pyramids. The image was acquired with the following parameters; V = -1.85 V; I = 0.85 nA.

possible approach is to combine FE calculations for the elastic term with *ab initio* density functional theory (DFT) data for the strain-dependent corrections to the (105) surface energy [55].

A further shape transition occurs between pyramids and larger islands, called *domes* [57–59]. The domes have a perfect fourfold symmetry as in the case of pyramids, but a more complex morphology, including four {105}, four {113}, and eight {15 3 23} facets (Figure 29.22e,f). It is reasonable to assume that domes are the result of the growth of pyramids beyond a critical size, at which a shape transition takes place. Such a transformation is still not fully settled, although the growth sequence of flat pyramid-stepped pyramid domes starting from the more relaxed top of pyramids seems favored from a kinetic view point [59]. Finally, dome islands may eventually dislocate and larger islands named "barns" [60] (Figure 29.22g,h) and "superdomes" with interfacial misfit dislocations appear, depending on the growth conditions [61–64]. We remark that the discussion has been limited here to pyramid shapes because their simple geometry was particularly suitable for the illustrative purpose of this chapter. The more complex shape of domes and barns is however easily accessible by FE simulations even within a full anisotropic material description.

29.4

Effect of Vicinality on the Shape of Quantum Dots

In this section, we aim at illustrating how much substrate vicinality allows a fine shaping of nanostructures in the Ge/Si(001) system. The complex miscutdependent nature of vicinal surfaces introduces the concept of asymmetry into the basic phenomena, leading to the formation and evolution of self-assembled QDs [65–67]. Besides its important implications for the growth process, asymmetry has a technological relevance, as it is potentially able to split degeneracy of QD states and provide optical anisotropy [68, 69]

If the cleavage plane is slightly misoriented from a high-symmetry (singular) plane, the surface breaks up into a staircase of terraces limited by steps, and is referred to as a *vicinal*. The relevant angles of the vicinal surfaces are the misorientation or miscut polar angle θ and the azimuthal angle ϕ (Figure 29.24). tan θ determines the step (number) density and tan ϕ the density of kinks on the step edge. For the sake of illustration, here we will consider the vicinal surface of Si(001) misoriented toward the [110] direction for which ϕ is zero. This corresponds to minimizing the density of surface kinks. Figure 29.25 shows the surface morphology of vicinal Si(001) surfaces at increasing miscut angles: it can be clearly seen that increasing the step density by increasing θ reduces the terrace width [70].

Several experimental studies have observed extended {105} faceting on Si(001) misoriented substrates [66, 71–76]. Therefore, the {105} energetics appears to be crucial in determining the morphological evolution of Ge islands on vicinal Si(001) surfaces.



Figure 29.24 Schematics of a surface vicinal to a high index surface. The density of steps and kinks is determined by the miscut polar angle θ and the azimuthal angle ϕ . *I* is the average distance between steps and *d* is the average distance between kinks.



Figure 29.25 STM images of vicinal Si(001) surfaces at increasing miscut angle: (a) $\theta = 2^{\circ}$; (b) $\theta = 4^{\circ}$; (c) $\theta = 6^{\circ}$; and (d) $\theta = 8^{\circ}$.

While on the flat Si (001) surface a {105} pyramidal island has a perfect fourfold symmetry and almost square base with each side oriented along the <010> directions (Figure 29.26a), it progressively elongates along the [110] direction as the substrate miscut gets higher, and its base becomes a distorted rhombus (Figure 29.26b–e).

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Miscut angle

Figure 29.26 Shape evolution of Ge islands on vicinal Si(001) surfaces. (a) $\theta = 0^{\circ}$; (b) $\theta = 1.5^{\circ}$; (c) $\theta = 2^{\circ}$; (d) $\theta = 4^{\circ}$; and (e) $\theta = 6^{\circ}$. From the schematics, it is evident that the perfect fourfold symmetry of square-based islands on the flat surface is broken by the miscut. The miscut-dependent asymmetry can be described in terms of the ratio between the lengths of the shortest (L_m) and the longest (L_M) island's sides.



Figure 29.27 Schematic representation of a {105} pyramid lying on a vicinal surface.

This shape evolution is accompanied by the increase in surface area of the facets along the step-down direction at the expense of the other two facets. In the following, we show that a strict correlation exists between the morphological evolution and the energetic factors that govern the {105} faceting at atomic scale.

Consider a simple geometric model of a {105} pyramid grown on a vicinal surface (Figure 29.27). The [551] intersection line of adjacent {105} facets forms an angle with the (001) plane (indicated as $\beta + \theta$ in the sketch), which is determined by the geometry of the facets and is equal to 8.05° [76]. To allow {105} faceting, this angle must never change, producing the observed elongation toward the miscut direction. By using elementary geometry, the expected miscut-dependent asymmetry in terms of the ratio between the longest and the shortest sides of the pyramid is straightforwardly calculated as

$$\frac{L_{\rm m}}{L_{\rm M}} = \sqrt{\frac{\csc^2 8^\circ + \csc^2 (8^\circ + \theta)}{\csc^2 8^\circ + \csc^2 (8^\circ - \theta)}}$$
(29.45)



Figure 29.28 L_m/L_M ratio as a function of the miscut angle. The filled dots are the experimental values measured from STM images, while the continuous line represents the expected analytical ratio for an ideal {105} pyramid calculated from Equation 29.45.

and shown in Figure 29.28 as a function of the miscut angle. The match between the analytical ratio obtained from Equation 29.45 (continuous line) and experimental data (full circles) is impressive, confirming that the problem of dot shape can be handled with the simple geometrical model.

The excess total free-energy change of the island with respect to a flat epilayer of Ge can be obtained from Equation 29.30 with proper allowance for the θ -dependence [77]

$$\Delta F(V,\theta) = [R(\theta) - 1]\rho_{\rm WL}V + [\gamma C_{\rm s}(\theta) - \sigma(\theta)C_{\rm B}(\theta)]V^{\frac{2}{3}}$$
(29.46)

Here, $C_{\rm s}(\theta) = S/V^{\frac{2}{3}}$ and $C_{\rm B}(\theta) = B/V^{\frac{2}{3}}$ are geometric factors which are simple increasing functions of the polar angle that can be calculated analytically; $\sigma(\theta) = \sigma \cos \theta + \beta \sin \theta$ is the surface energy density of the vicinal substrate, which can be estimated from the step formation energy per unit length $\beta = \sigma[1 - \cos(11.3^{\circ})]\csc(11.3^{\circ})$ [65]. For $\sigma = 60.5 \text{ meV} \text{\AA}^{-2}$, the specific surface energy of a 8° miscut surface is only slightly increased to 60.7 meV Å⁻², which is, for our purposes, a negligible correction.

The dependence of the relaxation factor on the miscut angle for a Ge{105} pyramid is easily assessed by FE simulations and the results are shown in Figure 29.29. To gain an insight into the effect of vicinality on QD's stability, we can make the simplifying assumption $\gamma = \sigma = 60.5$ meV Å⁻² and obtain, for a Ge{105} pyramid grown on misoriented substrates with θ ranging between 0 and 6°, the total energy versus volume curves shown in Figure 29.30.

The activation energy for island formation can be obtained by differentiating Equation 29.46 with respect to volume, giving

$$\Delta F^* = \frac{4}{27} \frac{[\gamma C_{\rm s}(\theta) - \sigma(\theta)C_{\rm B}(\theta)]^3}{(R-1)^2 \rho_{\rm WL}^2}$$
(29.47)



Figure 29.29 Relaxation factor computed by FE simulations for the different Ge island shapes observed on vicinal Si(001) surfaces.



Figure 29.30 Total free energy of Ge islands grown on vicinal Si(001) surfaces for different miscut angles. From the top to the bottom, the corresponding miscut angles are 0°, 6°, 1°, 5°, 2°, 4° and 3°.

It corresponds to the maximum value of ΔF at a given θ and the corresponding volume is the critical volume.

In Figure 29.31, the critical energy is plotted as a function of θ . One can see that the activation energy first decreases with the increase in the miscut angle, that is, the nucleation is easier on the vicinal substrate than on the flat substrate. The nearer the angle approaches 8.05°, the more the barrier increases, signaling that the formation of the pyramid is more and more unlikely. It must be noticed, however, that the activation barrier is strongly dependent on the value of the surface energy



Figure 29.31 Energy barrier for 3D island formation as a function of miscut angle.

Table 29.2 Strain-relaxed (for Ge epilayers of infinite thickness) surface energies (in meV Å⁻²) for Ge/Si surfaces of various orientations.

γ (001)62.44 ^a ; 60.7 ^b : 60.5 ^c γ (105)56.90 ^a ; 61.4 ^b γ (1 1 10)62.46 ^a	Surface orientation	Surface energies (meV Å ⁻²)
	γ(001) γ(105) γ(1 1 10)	62.44 ^{<i>a</i>} ; 60.7 ^{<i>b</i>} : 60.5 ^{<i>c</i>} 56.90 ^{<i>a</i>} ; 61.4 ^{<i>b</i>} 62.46 ^{<i>a</i>}

^aScopece *et al.* [78]. ^bLu *et al.* [79]. ^cLi *et al.* [80].

density γ of the {105} facets and a quantitative estimate would require taking into account the strain energy correction to the surface energy [55]. As a result of DFT in the local density approximation and semiempirical calculations, a number of fairly accurate surface energy values for the most relevant Ge/Si surfaces are available and are listed in Table 29.2. It is generally found that lowering the surface energy of the {105} facets under compressive strain flattens the activation energy and gives rise to the barrierless nucleation process, observed experimentally on the flat Si(001) surface [29–32].

Despite the approximations made in the analysis, the behavior of the activation energy displayed in Figure 29.31 indicates that the polar angle of 8° should be treated as a special case of {105} faceting. When the miscut angle is 8.05° , a pyramid can no longer form because the [551] line runs parallel to the substrate orientation (Figure 29.27) and the island rearranges itself into a strongly elongated prism of triangular cross section bounded by two adjacent {105} facets called *nanoripple* (Figure 29.32) [66, 75, 77, 81].

Its morphology is the result of cutting a $\{105\}$ pyramid along the [110] direction with a plane tilted by 8.05° from the (001) surface, that is, the vicinal Si (1 1 10)



Figure 29.32 (a) STM images of Ge ripples grown on the 8° miscut Si(001) surface. Note that, owing to the geometric constraint of vicinality, the downside of the ripple (enlarged view in panel (b)) cannot be bounded by {105} facets.



Figure 29.33 Geometry of a ripple as resulting from cutting a $\{105\}$ pyramid with a vicinal plane misoriented by an 8° angle with respect to the (001) surface.

plane. From the sketch shown in Figure 29.33, it is clear that, owing to geometric constraints, the downside of the ripple cannot be bounded by real facets and it gradually lowers in height and width as the number of stacked {105} layers decreases near the end of the island (Figure 29.32b). The ripple is almost a one-dimensional structure and it could be expected that the edge term neglected in Equation 29.46, being usually not significant in 3D nucleation, plays a sizable role. As a matter of fact, an accurate evaluation of the elastic, surface, and edge contribution to islanding for $\theta = 8.05^{\circ}$ shows that it is energetically more convenient to pile up material on an infinitely long ripple than to form an additional layer on the WL [82]. This explains the almost perfect alignment of ripples occurring on the Si (1 1 10) surface under Ge deposition (Figure 29.34).



Figure 29.34 $\,$ 3D STM image of the 8° miscut Si(001) surface being completely covered with Ge ripples.



the corresponding FPs are shown. The spots of the different facets are labeled as follows:



As islands grow, the morphology is no more just a skewed version of the symmetric shape on the flat substrate. As predicted by Spencer and Tersoff [65], topologically asymmetric islands appear in the shape sequence [77]. In comparison with the domes on the flat surface (Figure 29.35a), which have two symmetric [113] facets along the [110] direction (indicated by α in the corresponding FP), the domes grown on highly misoriented substrates have different set of facets (γ and γ') on the opposite sides (Figure 29.35b,c). FE calculations, made on 3D islands, show that the anisotropic shapes reflect the anisotropy of the elastic displacement field along the miscut direction [77].

In this context, an especially interesting surface is Si(111), on which Ge islands nucleate in the form of truncated tetrahedra with {111} and {113} facets.

On highly stepped vicinal surfaces, the anisotropic strain relaxation of Ge triggers the formation of islands directly from step-edge nanoprotrusions [83] (Figure 29.36). As the orientation of the (111) terraces coincides with a dominant low-energy facet, the protrusions propagate through the steps without disintegrating into other



Figure 29.36 STM images of the 5° miscut Si(111) surface at increasing Ge coverage: (a) 3.9 ML; (b) 4.3 ML; and (c) 4.8 ML.



Figure 29.37 Ge islands' aspect ratio as a function of miscut angle on vicinal Si(111) surfaces. The dashed line is the average surface misorientation $tan(\theta)$. As sketched in inset, the smaller the terrace width, the more pronounced the height of step protrusions.



Figure 29.38 (a-h) STM images of different stages of Ge island formation on the 1.5° miscut Si(111) surface. The images were taken at a nominal Ge coverage of 4.8 ML over an area of $\sim 20 \mu m^2$ of the sample. The [-1 -1 2] miscut direction is

indicated by arrows. (i) FE simulations of the in-plane strain tensor ε for 3D models of Ge islands based on the experimental geometry extracted from STM images. The white arrows indicate the direction of the island growth observed in the experiment.

facets, as occurs on vicinal Si(001) substrates, and grow in height following the misorientation of the substrate while advancing through the steps. As the average terrace width drops suddenly when the vicinal angle increases between 0 and 1° [83], step protrusions spread across many steps and, hence, become effectively 3D. Their aspect ratio is set by the average surface misorientation $\tan(\theta) \approx \theta$ (Figure 29.37). Therefore, Ge/Si islands acquire a characteristic huglike morphology which is controlled by the equilibrium strain field within the island and the substrate (Figure 29.38). Using the above-mentioned FE analysis, one finds that the growth is promoted along the rims but hindered in the center of the islands, explaining the appearance of the characteristic morphology.

29.5

Beyond the Elastic Relaxation: the Effect of Intermixing on Quantum Dot Nucleation

Here, we discuss some aspects of the epitaxial growth of QDs that go beyond the problem of elastic relaxation and were glossed over in the previous sections.

One point which has not been fully examined is what specific surface energy of the substrate σ has to be introduced in the free-energy balance of islanding (e.g., in Equations 29.29–29.43). In fact, it has been shown in Section 29.2 that the interface energy of a strained epilayer depends on the film thickness. Even ignoring the chemical contribution of interface energy in the case of coherent SK growth, in which the strained material wets the substrate before forming islands, one should include the effect of lattice distortion due to the misfit strain acting on the film. In principle, the task is not at all trivial and requires a detailed knowledge of the atomistic structure of surface atom bonding via first-principles calculations [79, 84]. Nonetheless, it has been recently proposed that the thickness dependence of the surface energy density of a growing film can be described by a simple analytical form, implying a nearly exponential decrease in the surface energy σ with the thickness *d* [80]

$$\sigma(d) = \sigma_{\rm s}^{\infty} + (\sigma_{\rm film}^{\infty} - \sigma_{\rm S}^{\infty}) \left(1 - e^{\frac{-d}{\eta}}\right)$$
(29.48)

In the previous relation, σ_s^{∞} is the surface energy of the bare substrate (e.g., of Si for Ge/Si), whereas $\sigma_{\text{film}}^{\infty}$ is that of the infinitely thick epilayer. For Ge/Si, it is found that Equation 29.48 nicely fits the *ab initio* data for $\eta = 1$: At low thickness (d < 2 ML), the correction is effective and surface energy drops from the value of the bare Si toward that of the bulk Ge deposit, slightly changing when Ge coverage is increased further. Therefore, for WL thickness between 3 and 4 ML of Ge, at which nucleation of 3D islands occurs [33], one can generally use the surface energy density of a strained infinite Ge film without altering significantly the total free-energy gain.

The energy gain of islanding is instead crucially altered by substrate-deposit alloying because, according to Equation 29.27, the volume strain energy density has a quadratic dependence on the misfit parameter. Therefore, a decrease in the lattice mismatch between the substrate and the growing layer is expected to lead to a substantial fall in the strain energy density. In these circumstances, intermixing of the Ge film with Si to form a Si_{1-x} Ge_x random alloy of average lattice mismatch f(x) = 0.04x and average composition x close to 0.50 [85, 86] is a highly favored process to reduce lattice mismatch [87]. As a direct experimental evidence of intermixing within the WL, we mention the buckled Ge dimer sites on Si(001) substrates observed by STM [88, 89].

It is an experimental fact that the equilibrium shape of the islands, as determined by the elastic field relaxation, is not excessively changed by intermixing at the typical temperatures used in growth experiments [90]. As a consequence, the effect of alloying may be viewed as a correction to the morphology predicted by the elastic FE analysis applied to unalloyed islands. One can consider, as a first approximation, a uniform alloy and use, according to the Vegard's law, elastic constants linearly interpolated between Si and Ge ones, namely,

$$C_{ij}(x) = C_{ij}^{\text{Ge}} x + C_{ij}^{\text{Si}}(1-x)$$
(29.49)

where C_{ij}^{Ge} and C_{ij}^{Si} are the stiffness tensors of pure Ge and Si, respectively (Table 29.1). Using the elastic constant and the lattice parameters of the alloy, we perform FE simulations of elastic relaxation of Si_{1-x} Ge_x islands of different aspect ratio *r* following the lines described in Section 29.3 but varying the Ge composition *x* between 0 and 1. The elastic energy density of each island is then compared to that of a Si_{1-x} Ge_x strained film of the same composition, which reads (Figure 29.39)

$$\rho_{\rm WL}(x) = \left\{ \frac{C_{11}(x) + C_{12}(x) - 2[C_{12}(x)]^2}{C_{11}(x)} \right\} [f(x)]^2$$
(29.50)

and the relaxation factor R(r,x) is computed. As evident from Figure 29.40, the scaling with the aspect ratio is only slightly dependent on the island's composition, being, in any case, nicely fitted by an exponential form $R(r,x) = e^{-k(x)r}$ [52]. The decay constant k(x) shows, in fact, a weak linear dependence on Ge composition



Figure 29.39 Elastic energy density of a flat Si_{1-x} Ge_x epilayer grown on Si as a function of the Ge content.



Figure 29.40 Relaxation factor versus aspect ratio for $Si_{1-x} Ge_x$ pyramids of different Ge content.



Figure 29.41 Dependence of the decay constant k(x) in Equation 29.43 on the Ge content x in the alloy.

(Figure 29.41). The decrease of the decay constant with Ge content is expected as Ge has somewhat smaller elastic constants than Si does (Table 29.1).

Taking into account the composition dependence in Equation 29.44, one can find the true path of the island's shape evolution, that is, the preferential aspect ratio for each volume, as a function of the alloying content (Figure 29.42). From the results, it is clear that in $Si_{1-x}Ge_x$ intermixed islands the morphological evolution toward a steeper island's shape is shifted to larger critical volumes depending on the Ge composition *x*. This finding matches experimental data [7, 91], and reveals that alloying cooperates/competes with shape change toward a complete elastic relaxation. As evident from Figure 29.18, the mechanisms described in Section 29.3 for pure Ge islands do not fully relieve the strain energy that remains concentrated at the bottom edges of the islands. In this context, the injection of Si atoms from the substrate, causing elastic energy relaxation to be also mediated by alloying, provides



Figure 29.42 Thermodynamically favored aspect ratio of Si_{1-x} Ge_x islands as a function of volume obtained by FE simulations.



Figure 29.43 Relative difference of relaxation factors between shallow (r = 0.05) and steep (r = 0.7) Si_{1-x} Ge_x islands as a function of the Ge content in the alloy.

a particularly efficient pathway toward strain relaxation. The second interesting observation comes from the comparison of the energy gain of 3D islanding as a function of the alloying, obtained by plotting the relative difference of relaxation factors $\Delta R/R$ between shallow (r = 0.05) and steep islands (r = 0.7) for different Ge compositions (Figure 29.43). As shown, Ge redistribution further broadens the free-energy gap between shallow and steep islands [92].

Despite the intriguing hints examined, the assumption of uniform alloying is not consistent with experimental results, which indicates, instead, relatively nonhomogeneous concentration profiles. Scattering experiments directly probing the composition map inside the islands, such as anomalous X-ray scattering at the K-edge of Ge at 11.103 KeV [90, 93] or X-ray scattering [94], find an increase in the average Ge content moving from the base toward the top, sometimes with a change of concentration at a given height. For instance, Wiebach *et al.* [94] report Ge concentrations of 25% in the lower and 30% in the upper part at about one-third



Figure 29.44 Diffuse scattering maps of (400) surface reflection for Ge domes using two different X-ray photon energies (a) 11.103 KeV (Ge K edge) and (b) 11.005 KeV. The intensity color scale is logarithmic. (c) and (d) are angular scans at constant radial position q_r corresponding to the dashed line in (a) and (b). Several fits corresponding to different lateral composition

profiles are shown for the scans carried out at 11.103 KeV (c) and 11.005 KeV (d). The corresponding Ge concentration profiles used in these fits are plotted at the inset. Reprinted with permission from A. Malachias, *et al.*, Phys. Rev. Lett, 91, 176101 (2003). Copyright 2003 by the American Physical Society.

of the island height, while Malachias *et al.* [90] find a Si-rich core covered by a Ge-rich external shell, as shown in Figure 29.44.

Different models (for a recent review, see [95]) have been considered, exploiting thermodynamic and/or kinetic factors as the driving force toward alloying. Nonetheless predicting both the equilibrium shape and composition of the dots remains a challenging task. However, if one neglects bulk diffusion and assumes that surface diffusion is fast, the concentration c(r, z) and the dot shape h(r) can be calculated in close form for a Ge island on Si(001) in the small-island limit [96]. The starting equations are the constitutive equations (Equation 29.40) for the stress with the inclusion in the diagonal components of the strain tensor ε_{ij} of a compositional strain $-\eta [c(r, z) - c_0]$ proportional to the expansion coefficient η of Ge within a WL film of negligible thickness and zero in the Si substrate. c_0 is the average composition of the island of volume V. Si_{1-x} Ge_x is taken as a fully miscible random alloy, a highly appropriate assumption for this system [97],

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the island surface having chemical potentials $\mu_i = dG_i/dc$ for each atomic species (*i* = Ge and Si), which also depend on the elastic strain and composition. The island shape is computed self-consistently through the equilibration condition, Equation 29.39, the nonuniform stress field resulting in a nonuniform composition along the surface. For a small island of low aspect ratio, the equilibrium *h*(*r*) and *c*(*r*, *z*) profiles can be disentangled, giving

$$h(r) = A\left[a_0 + \sum_{j=1}^{\infty} a_j J_0\left(\frac{z_j r}{R}\right)\right]$$
(29.51)

and

$$c(r,z) = C \left[\alpha + \frac{L}{r} \frac{\mathrm{d}}{\mathrm{d}r} \left(r \frac{\mathrm{d} h(r)}{\mathrm{d}r} \right) \right] \frac{z}{h(r)}$$
(29.52)

where J_0 is the zeroth order Bessel function and z_j is the *j*th zero of $J_1(z)$. *L* is a length scale factor and *C* sets the amount of strain-induced segregation that increases with the lattice misfit $\varepsilon = -\eta x$. As the island grows, the burial of successive layers with variable composition gives the scaled profiles depicted in Figure 29.45. From the composition map, it is evident that the large Ge atoms tend to segregate close to the apex of the island where the elastic strain is minimum, a feature that is often encountered experimentally. However, other authors [98, 99] have understood the observation of Si enrichment of the corners of faceted islands as an indication of relevant kinetic restrictions, which cannot be included in the above-mentioned simplified model.



Figure 29.45 Island shape and composition map according to Equation 29.52. The lateral size of the island is *L*. The composition map is a contour plot of the composition profile C/C_0 , the scaled deviation from a reference

composition C_0 . The step between contours is 0.25, vertical lines are the zero contours, and dark corresponds to the larger misfit component (i.e., Ge). Adapted from [96].

In principle, the concentration profiles minimizing the system free energy of the system may be obtained through atomistic Monte Carlo (MC) simulations [38, 100, 101] using an iterative procedure consisting of chemical-species random exchange, energy optimization, and acceptance probability determined by Boltzmann statistical weights. Nevertheless, a major limit to extensive application of this approach is the demanding computational cost when treating islands with realistic size/shape: note that a scaling-down approach is intrinsically limited by the need of reproducing facets with a minimum physically meaningful extension [92]. An interesting method for fast self-consistent calculation of SiGe distribution minimizing the elastic energy is based on a combined MC-FE approach [92, 102]. In the latter, an additional mesh is used to define a nonuniform composition grid, the values thereto assigned being randomly changed (maintaining constant the average composition) by an MC iterative procedure with an acceptance criterion based on the minimization of elastic energy at each step by FE calculations. This ensures that changes in the elastic field accompanying SiGe redistribution are correctly described in complex island's geometries. Even though the system evolution is supposed to be governed by thermodynamics only, this approach has been found to produce iso-composition maps closely matching that obtained by selective wet chemical etching [99] (Figure 29.46) for moderate growth temperature ($T \sim 580$ °C). Instead, the experimental tomographies for islands grown at higher temperature reveal composition profiles much more uniform than the simulated ones [92], thus revealing that kinetic effects cannot be neglected anymore in this growth regime. Thus, the development of methods capturing kinetics and thermodynamics altogether is required to simulate the actual dynamics of nanostructure evolution in the full range of growth temperature. To this end, a particularly promising approach, recently developed by Tu and Tersoff [103], has been able to qualitatively reproduce many striking phenomena observed experimentally in heteroepitaxial systems, even if for a simplified 2D model system.

29.6

Elastic Interaction between Ge Islands on Vicinal Si Substrates

The ultimate understanding of in-plane interactions of self-assembled nanostructures at surfaces is an urgent need for nanotechnology. In Section 29.4 we have shown that a fine shaping of Ge islands is possible on Si(001) by changing the miscut angle. This offers a direct way to alter the elastic-interaction potential among islands, which is greatly influenced by the detailed island's shape, and study the elastic interaction across a variety of realistic configurations of strain fields [67, 104].

The resulting effect depends on the intensity of the elastic field and, hence, on the island size. For small-volume islands (pyramids and ripples), the symmetry breaking of the elastic field induced by vicinality modifies the local spatial ordering of islands. For large multifaceted domes, the modified elastic pattern is able to



Figure 29.46 Atomic force microscopy (AFM) topographies showing the morphology of Ge islands grown on Si(001) before (left column) and after 10 min of 31% H_2O_2 etching (right column). The growth temperatures are 580 °C for (a) and (d), 600 °C for (b) and (e) and 620 °C for (c) and (f). The insets show a higher magnification (80 × 80) nm² of (d) the two different observed etched structures for pyramid islands, and (e) the protrusions in the ring structures of the

etched domes. The encircled islands in (d) are examples of pyramids without apex while the ones enclosed by squares correspond to pyramids with apex. The gray scale in (a-c) is related to the local surface slope while in (d-f) it represents a combination of local surface height and gradient so as to enhance small-scale morphological details. Reprinted with permission from A. Katsaros, *et al.*, Phys. Rev. B, 72, 195320 (2005). Copyright 2005 by the American Physical Society.

force the growth of Ge toward pathways completely different from those on the flat substrate.

Misfit islands interact repulsively through their mutual strain fields in the substrate [105, 106, 107]. Their mutual interaction energy Y is the extra energy density needed to create an island in a certain location when another island already exists nearby and is given by

$$Y = U(\mathbf{r}) - U(\infty) \tag{29.53}$$

where $U(\mathbf{r})$ is the total strain energy (per unit volume) stored in the substrate and in the islands for the relative position of the island pair defined by \mathbf{r} .

Figure 29.47a shows FE calculations of the elastic interaction energy for squarebased Ge pyramids on the flat Si(001) surface. For the two relevant configurations of an island pair, the interaction energy is almost isotropic. This is not the case with the Ge islands grown on vicinal substrates for which elastic interactions have a strong directional dependence (Figure 29.47b,c). When the misorientation angle is increased, the lowest energy configuration is achieved by aligning the pair along the [110] miscut direction. The latter configuration allows for a larger elastic relaxation



Figure 29.47 (a-c) Elastic interaction energy for different configurations of an island pair (a) on the flat, (b) on the 6° miscut, and (c) on the 8° miscut Si(001) surfaces (vertical axis in arbitrary units, horizontal axis in units of the average island side). The data in the panel (a) are fitted to a r^{-3} function at large island separations (dotted curve) and to an exponential function at short separations (dashed curve). The vertical line marks the boundary between the two regimes. Elastic energy density maps of an island pair on (d) 6° miscut and (e) 8° miscut surfaces. Each plot is displayed with two different scales giving the elastic relaxation within the islands and on the substrate around them.



Figure 29.48 Spatial distribution of nearest-neighbor distances of Ge islands on: (a) flat, (b) 1.5° miscut, (c) 2° miscut, (d) 4° miscut, (e) 6° miscut, and (f) 8° miscut Si(001) samples. The arrows indicate the [110] direction.

of the substrate in between the islands, as shown by the energy maps displayed in Figure 29.47d,e.

It is worth noting that, at large distances, where the actual shape of the island is immaterial, the elastic interaction can be described as the interaction between two concentrated distributions of dipoles and, thus, scales as r^{-3} [105] (dotted curve in (Figure 29.47a)). Conversely, the point-island approximation is inappropriate at smaller separations at which the exact details of the elastic energy curve strongly depend on the island's shape.

The anisotropy of strain field profiles inside and around each island modifies the local spatial organization of Ge nanostructures. By measuring the spatial distribution of nearest-neighbor distances (SDNN) on different vicinal substrates, it is found that the local arrangement of islands becomes anisotropic with an increasingly miscut angle (Figure 29.48).

The SDNN is calculated from a systematic analysis of STM images. First, the centers of mass of all islands are identified. Then, for each island, the nearest neighbor is found by calculating the distances between the corresponding centers of mass. Each panel in Figure 29.48 shows the position of the nearest neighbors measured on the related vicinal substrate. It can be seen that the relative density of nearest neighbors (given by the color scale) is almost isotropic for flat substrates, whereas it is markedly increased along the [110] direction at high miscuts. Thus, the morphological anisotropy of islands at high misorientation angles breaks the isotropy of elastic potential, producing directions of reduced elastic interaction energy. As long as the volume of islands is small (e.g., for pyramids and ripples), the effect of elastic anisotropy on Ge/Si heteroepitaxy is limited to short-range local ordering interactions. Nonetheless, the much more intense elastic interactions between Ge domes can also be tuned with substrate vicinality. Figure 29.49a shows the island's interaction energy calculated for a pair of Ge domes grown on the flat Si(001) surface; the corresponding contour plot is reported in Figure 29.49b. The interaction potential reflects the fourfold symmetry of the island and results in an energetic barrier to island coalescence with local minima around the <001> directions. The shape of the interaction energy surface is strongly modified for the domes on the vicinal substrate (Figure 29.49c,d). The breaking of the island's symmetry induced by substrate vicinality produces directions along which islands can get into contact with low elastic repulsion. Specifically, elastically soft configurations are achieved for islands interacting within an angular window of approximately $\pm 60^{\circ}$ about the [110] miscut direction (Figure 29.49d). This modified elastic pattern orients Ge/Si heteroepitaxy toward an extended coalescence regime in which the impingement directions are dictated by the shape of the elastic potential. STM images clearly show that extensive coalescence occurs on 8° and 10° miscut Si(001) surfaces (Figure 29.50). Moreover, along the elastically soft directions around [110], the number of impingements is impressively higher, as shown by a statistical analysis of the distribution of impingement directions of domes grown on highly misoriented substrates (Figure 29.49e,f). This indicates that the elastic interaction anisotropy is the main driving force for the observed growth evolution of Ge on vicinal surfaces. The experimental evidence that the



Figure 29.49 (a) Interaction energy surface of Ge domes on the flat Si(001) surface and (b) corresponding contour plot. (c) Interaction energy surface of Ge domes on 10° miscut Si(001) surface and (d) corresponding contour plot (The region of reduced

interaction energy around the miscut direction is highlighted). Angular distribution of impingement directions measured (e) on 8° miscut Si(001) substrates and (f) on 10° miscut Si(001) substrates.

symmetry breaking of the elastic field can be used to effectively direct the pathway of Ge heteroepitaxy lays the groundwork for new self-assembling strategies designed to suit the natural shape of the elastic interactions among nanostructures. Finally, this analysis is readily applicable to other heteroepitaxial systems for which the elastic field is a common key parameter.



Figure 29.50 STM images showing the extended coalescence regime of domes (a,b) on the 8° miscut and (c,d) on the 10° miscut Si(001) surfaces.

29.7 Summary

We have presented a short illustration of the basic concepts related to the epitaxial growth of semiconductor QDs through a critical analysis of a few experimental and theoretical aspects concerning Ge on Si(001). Owing to its simplicity and ongoing interest for device applications, this system can be regarded as a model one in heteroepitaxy. First, we have obtained the classical Bauer criterion for the equilibrium of small 3D clusters with the parent phase following the atomistic approach of Stranski and Kaischew, which introduces the concept of mean separation work. Then we derive the thermodynamic condition for the occurrence of planar growth and clustering from the dependence of the Gibbs free energy and chemical potential on the thickness of the adsorbed layer.

Then the stability of QD morphology is examined. The relaxation of the bulk and surface elastic strain is illustrated in the framework of continuum elasticity theory and useful analytical formulas applicable to simple morphologies are given. The results of modeling are compared with the experimental STM data taken on SiGe as a function of coverage to assess the validity of model descriptions against realistic growths. In this context, we consider in Section 29.4 the effect of substrate symmetry – that is, crystallographic orientation, steps, and vicinality – on QD shape and stability. In Section 29.5, we address the problem of intermixing starting from homogeneous alloying and then shifting to more realistic compositional maps. In the last section, we present results on the control of elastic interactions between dots and on their effect on lateral ordering. A variety of realistic configuration of strain fields is analyzed.

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