Thermodynamic driving force of formation of coherent three-dimensional islands in Stranski-Krastanov growth

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The formation of coherent three-dimensional (3D) islands in highly mismatched epitaxy is discussed in terms of the traditional concept of wetting. It is shown that the wetting layer and the 3D islands represent different phases which cannot be in equilibrium with each other. The transfer of matter from the stable wetting layer to the 3D islands is thermodynamically unfavored. The experimentally observed critical misfit for coherent 3D islanding to occur and the coexistence of pyramids with discrete heights of two, three, four, . . . , monolayers can be explained assuming that the thermodynamic driving force of formation of coherent 3D islands on the surface of the wetting layer of the same material is the reduced average adhesion of the islands to that layer and that the islands height is a discrete variable.

The growth of thin epitaxial films usually takes place far from equilibrium. Nevertheless, thermodynamic considerations are a necessary step for understanding of the process. Of particular interest is the thermodynamic driving force (TDF) which is responsible for one or another mechanism of growth. While this question is well understood in terms of wetting of the substrate by the overgrowth in the cases of island or Volmer-Weber (VW) growth and layer-by-layer or Frank–van der Merwe (FM) growth,[1–3] the Stranski-Krastanov (SK) growth [three dimensional (3D) islands on top of a thin wetting layer] is far from being clarified. The reason is that the SK growth is in fact a growth of material A on the same material A, which thermodynamically requires the formation and growth of 2D rather than 3D islands. This is particularly true in the case of the *coherent* Stranski-Krastanov growth,[4] where dislocation-free 3D islands are strained to the same degree as the wetting layer.[4–6] This is the reason why it is widely accepted that the energy of the interfacial boundary between the 3D islands and the wetting layer is equal to zero.[7] Although this energy is expected to be small compared with that of the free crystal faces,[8] it should not be neglected since this is equivalent to the assumption that the islands wet completely the wetting layer. The latter rules out 3D islanding from a thermodynamic point of view.[9]

The need for a thermodynamic analysis arises also from the experimental observations of a critical misfit for coherent 3D islanding to occur,[10–13] and the simultaneous presence of islands of different thickness which vary by one monolayer.[14,15] The existence of a critical misfit, as well as of stable two, three or four monolayers thick islands, do not follow from the tradeoff[7,8]

$$\Delta E \approx C' \gamma V^{2/3} - C'' \varepsilon_0^2 V \qquad (1)$$

between the cost of the additional surface energy and the gain of energy due to the elastic relaxation of the 3D islands relative to the wetting layer (V, γ, and ε_0 are the islands

volume, the specific surface energy and the lattice misfit, respectively, and C' and C'' are constants).

It was recently suggested that the TDF for coherent 3D islanding is the incomplete wetting of the substrate by the islands,[16] rather than the elastic relaxation of the material in the islands. The incomplete wetting is due to the displacements of the atoms near the island edges from the bottoms of the corresponding potential troughs provided by the wetting layer. This results in a series of critical volumes at which the monolayer high islands become unstable against the bilayer islands, the bilayer islands against the trilayer islands, etc. The misfit dependence of the first critical size N_{12} for the monobilayer transformation displays a critical behavior in the sense that coherent 3D islands can be formed at a misfit higher than some critical value. Below this value the film should grow in a layerlike mode until misfit dislocations are introduced to relieve the strain. However, the approximation used by the authors, which is based on the 1D model of Frenkel and Kontorova,[17,18] was unable to describe correctly the individual behavior of atoms inside each layer, since it assumes a potential with a period given by the average of the separations of atoms (considered frozen) in the layer underneath. Although this model gives qualitatively reasonable results concerning the energy of the islands, it is inadequate to calculate, in particular, the average adhesion energy of the islands to the wetting layer.

In the present report we recollect some simple thermodynamic aspects of the epitaxial morphology based on the traditional concept of wetting and consider the coherent SK growth from this point of view. The same concepts were in fact advanced by Stranski in his model, admittedly very peculiar, of a monovalent ionic crystal K^+A^- on the surface of an isomorphous bivalent crystal $K^{2+}A^{2-}$.[19] We then support our thermodynamic considerations by numerical calculations making use of a simple minimization procedure on the same atomistic model in $1+1$ dimensions (length+height) as in Ref. 16. The 3D islands are represented by linear chains of

atoms stacked one upon the other,[18] the islands height being thus considered as a discrete variable which increases by unity from one. The latter is of crucial importance as the aspect ratio of the 3D islands is usually of the order of 0.1 and the height is of the order of 10 monolayers.[5,6] The atoms interact through an anharmonic Morse potential

$$V(x) = V_0 [e^{-12(x-b)} - 2e^{-6(x-b)}]. \quad (2)$$

The total interaction energy as well as its derivatives with respect to the atomic coordinates, i.e., the forces, are calculated. Relaxation is then performed iteratively by allowing the atoms to displace in the direction of the forces until these fall below some negligible cutoff value. We consider interactions in the first coordination sphere in order to mimic the directional bonds that are characteristic for semiconductors.[20] Inclusion of further coordination spheres alters only minimally the numerical results. The substrate (the wetting layer) is assumed to be rigid.

A mother phase (a vapor) and a new phase (e.g. a strained planar film or unstrained 3D crystals) are in equilibrium with each other when their chemical potentials are equal. A transition from one phase (mother or new) to another takes place when the chemical potential of one of the phases becomes smaller than that of the other. The TDF for this transition is the difference of the chemical potentials of both phases at the given pressure and temperature. The TDF which determines the occurrence of one or another mechanism of epitaxial growth (growth from vapor of a strained 2D layer or 3D islands) is the difference $\Delta\mu = \mu(n) - \mu_{3D}^0$ of the chemical potential $\mu(n)$ of the overlayer which depends on the film thickness measured in number n of monolayers counted from the interface, and the chemical potential μ_{3D}^0 of the bulk 3D crystal of the same material.[2,3] The thickness dependence of $\mu(n)$ originates from the thickness distribution of the misfit strain and, on the other hand, from the interaction between the deposit and the substrate, which rapidly decreases with the distance from the interface ($E_{AB} \rightarrow E_{AA}$).[2,21]

If we deposit a crystal A on the surface of a crystal B, $\Delta\mu$ can be written in terms of the interatomic energies per atom, E_{AA} and E_{AB}, required to disjoin a half-crystal A from a like half-crystal A and from an unlike half-crystal B, respectively:[22]

$$\mu(n) = \mu_{3D}^0 + [E_{AA} - E_{AB}(n)] = \mu_{3D}^0 + E_{AA}\Phi. \quad (3)$$

The adhesion energy E_{AB} includes in itself the thickness distribution of the strain energy and the attenuation of the bonding with the substrate. $\Phi = 1 - E_{AB}/E_{AA}$ is the *adhesion parameter* which accounts for the wetting of the substrate by the overgrowth. Equation (3) is equivalent to the familiar 3-σ criterion of Bauer.[1,21]

As follows from Eq. (3) the parameter $\Phi = \Delta\mu/E_{AA}$ is equal to the TDF for occurrence of one or another mode of growth relative to the cohesive energy E_{AA}. In the two limiting cases of VW ($0 < \Phi < 1$) and FM growth ($\Phi \leq 0$, $\varepsilon_0 \approx 0$), $\Delta\mu$ tends asymptotically with increasing film thickness to zero from above and from below, respectively, but changes its sign in the case of SK growth ($\Phi < 0, \varepsilon_0 \neq 0$), as shown in Fig. 1.[3,21] Consider now Fig. 1 in terms of equilib-
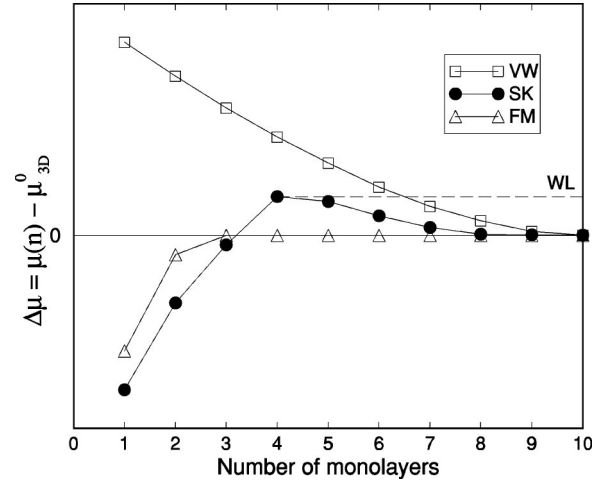

FIG. 1. Schematic dependence of the film chemical potential on the film thickness in number of monolayers for the three modes of growth: Volmer-Weber (VW), Stranski-Krastanov (SK), and Frank–van der Merwe (FM). The dashed line gives the chemical potential of the unstable wetting layer.

rium vapor pressures instead of chemical potentials. Although the connection is straightforward ($\mu \propto \ln P$) such a consideration gives a deeper insight into the problem.[19] Thus, as long as $\mu(n) < \mu_{3D}^0$ a thin planar film can be deposited at a vapor pressure P that is smaller than the equilibrium vapor pressure, P_0, of the bulk crystal, but is larger than the equilibrium vapor pressure P_1 of the first monolayer, i.e., $P_1 < P < P_0$. In other words, a planar film can be deposited at *undersaturation* $\Delta\mu = kT \ln(P/P_0)$ with respect to the bulk crystal. The formation of 3D islands [$\mu(n) > \mu_{3D}^0$] requires $P > P_0$, or a *supersaturation* with respect to the bulk crystal.

Applying the above considerations to the SK growth leads unavoidably to the conclusion that the 3D islands and the wetting layer represent necessarily different phases and thus have different chemical potentials. The reason is that the two phases are in equilibrium with the mother phase (the vapor) under different conditions which never overlap. The wetting layer can be in equilibrium only with an undersaturated vapor phase, while small 3D islands can be in equilibrium only with a supersaturated vapor phase. The dividing line is thus $\Delta\mu = kT \ln(P/P_0) = 0$ at which the wetting layer cannot grow thicker and the 3D islands cannot nucleate and grow. Hence the wetting layer and the 3D islands can never be in equilibrium with each other.

It follows from the above that the derivative $d\Delta E/dV$ of the energy of the 3D islands relative to that of the wetting layer, gives the difference of the chemical potentials of the wetting layer (the dashed line in Fig. 1) and the chemical potential of the 3D islands. In other words, it represents the difference of the supersaturations of the vapor phase with respect to the wetting layer and the 3D islands. As the thickness and the energy of the wetting layer depend on the misfit it would be more suitable if one chooses as a reference the bulk crystal rather than the wetting layer.[23] Transfer of material from the stable wetting layer ($\mu_{WL} < \mu_{3D}^0$) to the 3D islands is connected with increase of the free energy of the system, and therefore, is thermodynamically unfavored. A
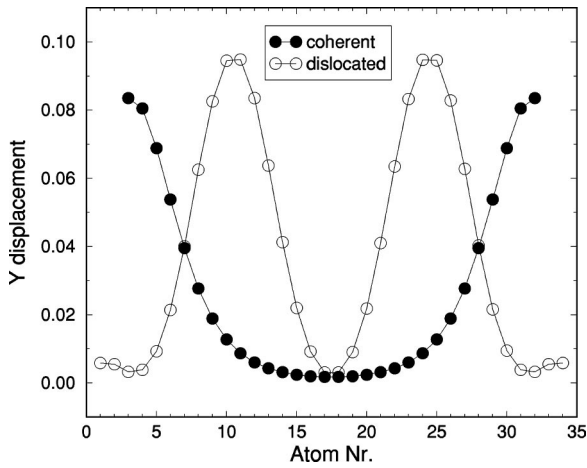
FIG. 2. Vertical displacements of the atoms of the base chain of a coherent (a) and a dislocated (b), 3-monolayer-thick island, given in units of the lattice parameter of the wetting layer and measured from the bottoms of the potential troughs provided by the homogeneously strained wetting layer. The misfit ε_0 amounts to 7% and the islands contain 30 and 34 atoms in their base chains, respectively.

planar film thicker than the stable wetting layer is unstable and the excess of the material can be transferred to the 3D islands if the necessary thermal activation exists.

We focus our attention on the adhesion between the 3D islands and the wetting layer. Figure 2 is an illustration of the difference (and resemblance) between the classical and the coherent SK mode. In the calculations, the sizes of the base chain of the island (30 and 34 atoms, respectively) have been chosen just below and above the critical size for introduction of misfit dislocations at the given misfit of 7%. As seen, in both cases the 3D islands lose contact with the wetting layer. The vertical displacements are largest at the chain's ends in the coherent SK mode and around the dislocation cores in the classical case, but the physics is essentially the same. The
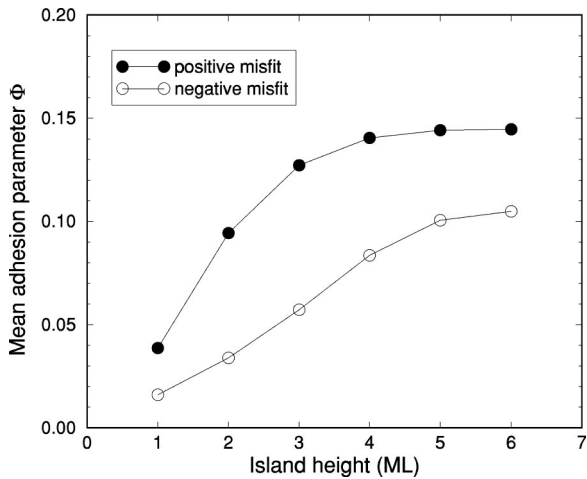
FIG. 3. Mean adhesion parameter Φ as defined by Eq. (1) as a function of the islands' height in number of monolayers for positive and negative values of the misfit of absolute value of 7%. Coherent islands of 14 atoms in the base chain were considered in the calculations.
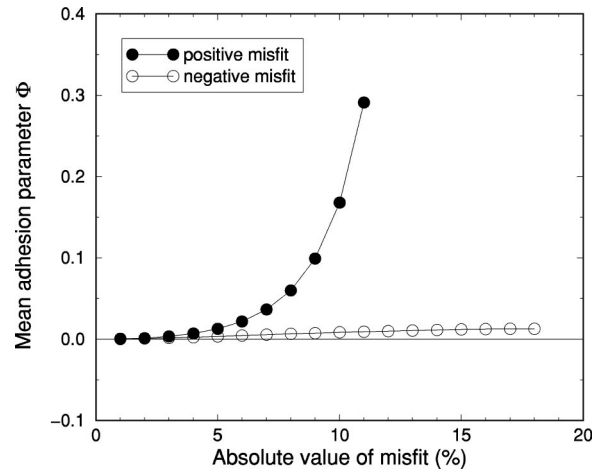
FIG. 4. Mean adhesion parameter of one monolayer high, coherent islands as a function of the lattice misfit. The islands contain 20 atoms. Data for both positive and negative misfits are shown in one quadrant for easier comparison.

mean adhesion parameter Φ increases with the islands' height and saturates beyond several monolayers (Fig. 3). In our model, Φ is calculated as the adhesion energy between island and wetting layer at the given misfit (7%) minus the corresponding value for zero misfit. It can be seen that the compressed overlayers exhibit a greater tendency to coherent SK growth than expanded ones as expected, due to the anharmonicity of the potential (2).

The same tendency is seen more clearly in Fig. 4 which shows in fact the dependence of the TDF for formation of coherent 3D islands $\Delta\mu$ on the lattice misfit. The latter remains close to zero for expanded overlayers but increases steeply beyond approximately 5% in compressed overlayers. This behavior agrees well with the misfit dependence of the critical size N_{12} for the monobilayer transformation to occur, as shown in Fig. 5, where a steep rise of N_{12} with decreasing absolute value of the misfit is observed only in compressed overlayers. Note that it is less sharp for expanded ones opposite to earlier finding.[16]
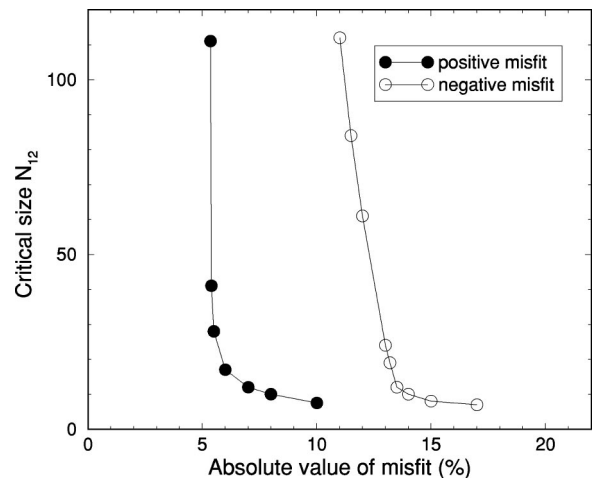
FIG. 5. Misfit dependence of the critical size N_{12} (in number of atoms) for positive and negative values of the lattice misfit. The curves are shown in one quadrant for easier comparison.

We discuss now the discrete character of the height of the 3D islands. The experimentally observed volume of the quantum dots varies roughly from 20 000 to 50 000 atoms.[6,11] Typical values of the aspect ratio of the islands height and half-base are of the order of 0.1.[6,24] Thus a pyramid with a base edge of 100 atoms and aspect ratio 0.1, and containing 22 000 atoms, is only 5 monolayers high. The addition of 14 400 atoms (a new base plane of 120×120 atoms) requires only one more atomic plane. Calculations of the energy of islands having a shape of a frustum of a pyramid are usually performed assuming implicitly that the lengths of the lower R and upper R' bases, and in particular the height h, are continuous variables. Equation (1) is obtained by using the Tersoff approximation which neglects the gradient of strain in a direction normal to the surface plane together with $h \ll R$,[7] and assuming $h \gg c$ where c is the atomic distance.[8] This would be correct if the crystals contain at least several million of atoms.

We conclude that the wetting layer and the 3D islands represent different phases which cannot be in equilibrium with each other, and the SK morphology is a result of the replacement of one first order phase transition (vapor-wetting layer) by another first order transition (vapor-3D islands). The transfer of matter from the stable wetting layer to the 3D islands is thermodynamically unfavored. The experimental observations mentioned above can be explained on the base of two assumptions: the thermodynamic driving force for the coherent 3D islanding is the incomplete wetting and the height of the 3D islands is a discrete variable varying by one monolayer. This leads to the results that (i) monolayer high islands with a critical size appear as necessary precursors for 3D islands, (ii) the 2D-3D transition takes place through a series of intermediate states with discretely increasing thickness that are stable in separate intervals of volume (see Refs. 14,15), (iii) there exists a critical misfit below which coherent 3D islands are thermodynamically unfavored (see Refs. 10–13) and the misfit is accommodated by misfit dislocations at a later stage of the growth. Compressed overlayers show a greater tendency to 3D clustering than expanded ones, in agreement with experimental results.[10] Result (i) explains readily why the volume distribution of InAs/GaAs self-assembled quantum dots agrees well with the scaling functions for two-dimensional submonolayer homoepitaxy model.[25]

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