Shape Transition in Growth of Strained Islands

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Strained islands formed in heteroepitaxy sometimes change shape during growth. Here we show that there is typically a first-order shape transition with island size, with the discontinuous introduction of steeper facets at the island edge. We present a phase diagram for island shape as a function of volume and surface energy, showing how surface energy controls the sequence of island shapes with increasing volume. The discontinuous chemical potential at the shape transition drastically affects island coarsening and size distributions. [S0031-9007(99)08789-X]

The nucleation and growth of three-dimensional clusters or "islands" on a surface has long been a central issue in surface physics [1–3], because such islands represent a common mode of growth in heteroepitaxy. Recently there has been renewed interest in island growth. In particular, such islands are candidates for "self-assembled quantum dots," which have been proposed as building blocks for optoelectronic devices, cellular automata, and other nanoscale devices [4,5].

There is a well-developed understanding of island nucleation [6] and subsequent coarsening (Ostwald ripening) [7] for the simple case where islands grow with a fixed shape. But in several cases, bimodal island-size distributions have been observed, inconsistent with classic coarsening [8–11]. Recently it has been shown that the bimodal size distribution is directly related to a change in shape of the growing islands [10]. The precise nature of this shape transition has been the subject of some discussion [10,11]. But it is clear that the shape change is closely related to the problem of obtaining uniform island-size distribution [11], a key issue for potential applications of these islands in nanoscale devices.

Here we study the equilibrium shape of strained islands, and their shape evolution with increasing size. The analysis treats fully faceted islands with fixed facet slopes [12], as are expected [6] and observed [10] at typical growth temperatures. We treat the problem in two dimensions (2D), but all the key results carry over directly to 3D [13], as discussed below.

Our analysis reveals the existence of a first-order shape transition at a critical island size. At the transition, steeper facets of finite size are introduced at the island edges, and the overall aspect ratio (height/width) increases discontinuously. The existence and type of transition depends on the relative slopes and surface energies of the different facets. We present a phase diagram describing all possible sequences of island shape transitions within the model.

This discontinuous transition plays an essential role in the anomalous coarsening [11] and bimodal size distribution [10,11] observed during island growth. Moreover, the

introduction of steeper facets plays a key role in the subsequent introduction of dislocations [14]. Thus an understanding of the shape transition is essential to the larger picture of growth and relaxation of islands.

We focus on the case of an island formed on top of a wetting film (Stranski-Krastanow growth), as for Ge on Si or InAs on GaAs. The analysis is also applicable to nonwetting systems such as Si on Ge, and many of the qualitative results carry over with minor modification, as discussed below.

Figure 1 illustrates our notation for the island shape: the *projected* facet lengths for the top, shallow, and steep facets are L_0, L_1, and L_2, respectively; and the corresponding slopes are $s_0 = 0$, s_1, and s_2. To obtain the equilibrium shape, we minimize the energy with respect to facet lengths under the constraint of fixed volume. (We have also considered asymmetric shapes, including a steep facet on only one side; but in each case we examined, the symmetric shape is preferred.)

The energy is defined relative to a coherently strained planar layer. The extra surface free energy due to island formation is

$$E_s = 2\Gamma_1 L_1 + 2\Gamma_2 L_2. \qquad (1)$$

Here $\Gamma_n = g_n(1 + s_n^2)^{1/2} - g_0$ is the extra energy for facet n, per projected length; and g_0, g_1, and g_2 are the surface free energies per unit length for the top, shallow, and steep facets, respectively. We assume that the top facet has the same surface energy as the wetting film on which the island grows. (The film-substrate interface
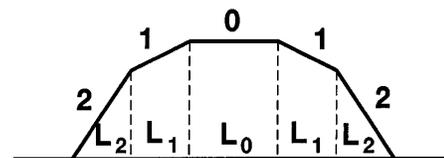

FIG. 1. Schematic representation of the 2D island with three types of facets: top (0); shallow (1); and steep (2). The projected facet lengths are L_0, L_1, and L_2, respectively.

covers the entire sample, so it contributes only an irrelevant constant energy.)

Island formation allows some elastic relaxation relative to the planar system, lowering the energy. In the shallow-island approximation [15], the elastic relaxation energy can be expressed as a double integral over the island

$$E_r = c \lim_{a \to 0} \int \int s(x)s(x') \ln \left| \frac{x - x'}{a} \right| dx\, dx'. \quad (2)$$

Here x is the position along the island; $s(x)$ is the local slope; and $c = \sigma_b^2(1 - \nu)/2\pi\mu_s$, where σ_b is the xx component of the bulk misfit stress, ν is the Poisson ratio, and μ_s is the shear stress modulus of the substrate. We neglect the contribution of surface stress [16]. The integral can be evaluated analytically for each facet pair, giving E_r as a function of s_1, s_2, L_1, L_2, and V, where V is the (2D) island volume.

To reduce the number of parameters, we introduce a characteristic length $L_c = |\Gamma_2|/cs_1^2$, energy $E_c = |\Gamma_2|L_c$, and volume $V_c = L_c^2$. The island energy $E = E_s + E_r$ can then be written in the dimensionless form

$$\varepsilon(v, r, s, \lambda_1, \lambda_2) = v^{1/2}\varepsilon_s(r, \lambda_1, \lambda_2) - v\varepsilon_r(s, \lambda_1, \lambda_2). \quad (3)$$

Here $\varepsilon = E/E_c$; $v = V/V_c$; $r = \Gamma_1/\Gamma_2$ is a dimensionless measure of the relative surface energies; $s = s_2/s_1$ is the ratio of facet slopes; and $\lambda_1 = v^{-1/2}L_1/L_c$ and $\lambda_2 = v^{-1/2}L_2/L_c$ characterize the dimensionless shape. After scaling, the island is described by two material parameters (r and s) and three size/shape parameters (v, λ_1, and λ_2).

For a given volume, the equilibrium shape (λ_1, λ_2) of the island is that which minimizes its free energy:

$$\varepsilon_v(v, r, s) = \min_{\lambda_1, \lambda_2} \varepsilon(v, r, s, \lambda_1, \lambda_2). \quad (4)$$

As long as growth or coarsening is slow compared to the time scale for internal shape changes, the island will have its equilibrium shape and energy ε_v.

These energy-minimizing shapes are shown in Fig. 2 for a typical case: $s = 2$, $r = 0.2$, $\Gamma_2 > 0$. At the smallest volumes there is no island at all; all the material remains in the planar wetting layer. Above a lower transition volume the island is stable, and consists of shallow side facets and a top facet. As the volume increases, the top facet shrinks. Then at an upper transition volume, the shape changes discontinuously with the appearance of steep facets. With further size increase, the shallow and top facets both continue to shrink.

This sequence of transitions is not universal; it depends on the surface energies via r. Viewing each type of island (each distinct combination of facets) as a phase of the system, we can calculate a phase diagram, giving the phase versus v and r. Because our scaling is based on $|\Gamma_2|$, the complete phase diagram includes two cases, $\Gamma_2 > 0$ and
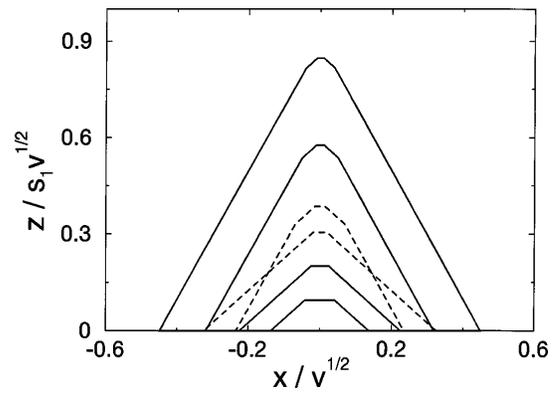

FIG. 2. Minimum-energy island shapes at different volumes, for $s = 2$, $r = 0.2$, and $\Gamma_2 > 0$. The volumes shown are $v = 0.017$ (the smallest size at which an island occurs in equilibrium), 0.05, 0.105 (two dashed islands), 0.2, and 0.4. The two dashed islands show the (energetically degenerate) shapes just before and after the shape transition at $v = 0.105$.

$\Gamma_2 < 0$. These are shown in Fig. 3, for the case $s = 2$. (The topology of the phase diagram does not depend on s, but s does affect the positions of the transitions as noted below.)
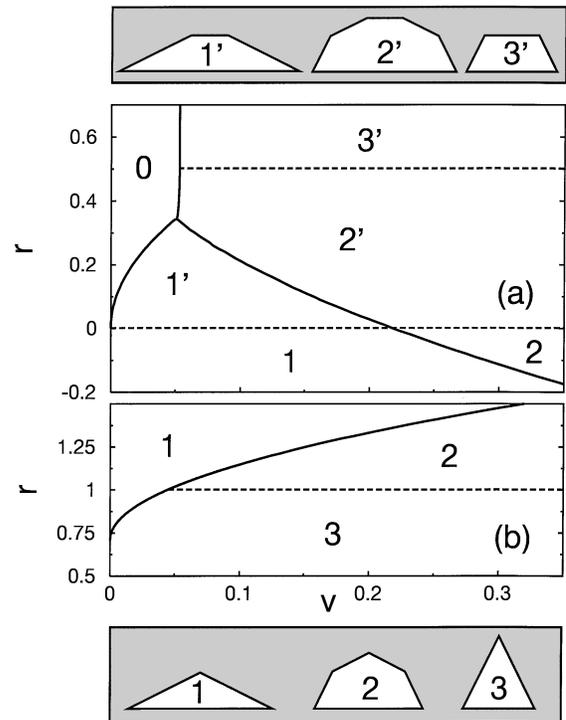

FIG. 3. Phase diagram (in two parts) showing island type vs volume v and surface energy parameter r. Six distinct island shapes occur, having the following: (1) shallow facet only; (2) shallow and steep facets; (3) steep facet only; (1') shallow and top; (2') shallow, steep, and top; and (3') steep and top. Phase (0) corresponds to the uniform flat film. The two cases are (a) $\Gamma_2 > 0$, and (b) $\Gamma_2 < 0$. Solid curves describe first-order phase transitions, while the horizontal dashed lines are second order.

The case of principal interest is $\Gamma_2 > 0$. In that case five different island shapes occur, defined by the presence or absence of the three types of facets (top, shallow, and steep). The behavior can be divided into distinct regimes, according to the value of r.

Regime I, $r < 0$.—There is no barrier for island nucleation when $r < 0$. Even the smallest island is stable, relative to a uniform layer, because the surface energy of the planar film is higher (per projected area) than the surface energy of the shallow facet. In this case the top facet never appears at any volume. With increasing volume, there is a transition from a pyramidal shape with only shallow facets, to a shape with both shallow and steep facets.

Regime II, $0 < r < r_{c1}$.—At higher facet energy, islands nucleate only at a finite volume. So with increasing volume, there is a transition from planar layer to shallow-faceted island, and then a second transition where the steep facets appear. The parameter r_{c1} is defined by the triple intersection in Fig. 3a.

Regime III, $r_{c1} < r < r_{c2} = 1/s$.—For still larger r, the steep facet is already present for the smallest island which is stable (relative to the planar layer). Once the island nucleates, there are no further shape transitions.

Regime IV, $r_{c2} < r$.—The surface energy of the shallow facet is so high relative to the steep facet that the shallow facet is never favorable. The island nucleates with only steep and top facets, and there is no subsequent shape transition.

The horizontal line at $r = 0$ represents a transition between shapes with and without a top facet. Similarly r_{c2} separates states with and without a shallow facet. These transitions are second order; i.e., the top or shallow facet appears or disappears continuously at the transition.

For the second case, $\Gamma_2 < 0$, the phase diagram is simpler. Three distinct regimes occur and islands are present at any nonzero volumes.

Regime I, $r < 1/s^{1/2}$.—Because of the higher shallow-facet surface energy, only steep-faceted islands form, with no shape transition.

Regime II, $1/s^{1/2} < r < 1$.—At lower shallow-facet energies, small islands are shallow-faceted, with a transition to steep-faceted at larger size.

Regime III, $r > 1$.—At even lower shallow-facet energy, the transition is from shallow-faceted to shallow-and-steep; the shallow facet is present at all volumes.

We emphasize that, while the calculations were performed for a 2D model, the key results all hold for islands in 3D as well (at least for typical symmetric shapes). The shape transitions remain first order with volume and second order with r; the transition values of r are the same in 3D as in 2D; and the topology of the phase diagram remains valid in 3D.

Within our model, the top facet is always present if $\Gamma_1 > 0$ and $\Gamma_2 > 0$, for 3D as well as 2D. This seems to contradict observations that in equilibrium, small Ge or SiGe islands on Si(001) are (105)-faceted pyramids.

However, Fig. 2 (and prior work [17]) shows that the top facet shrinks rapidly with increasing island size, so even if present in equilibrium, it might be difficult to observe. In fact, in recent *in situ* scanning tunneling microscopy experiments [18], all such islands examined at sufficient resolution show small (001) top facets as predicted here.

Very small SiGe islands on Si(001) have been reported to have an aspect ratio lower than for (105) pyramids [19]. The presence of a top facet which shrinks with increasing island size would provide a natural and consistent explanation of this observation.

In Fig. 4 we plot the island energy versus volume for $s = 2$, $r = 0.2$, and $\Gamma_2 > 0$, to illustrate the energetics of the shape transition and the relative importance of the top facet. The lines 1' and 2' correspond to an island with and without a steep facet. They cross at a transition volume v_t corresponding to the shape transition.

However, if we artificially exclude the top facet, the change in energy can be quite small, with little effect on v_t. This is shown by the long-dashed lines 1 and 2 in Fig. 4. Thus minor effects neglected here might conceivably suppress the top facet. For example, there may be an "edge energy" associated with the boundary between two facets. A similar but size-dependent term can arise from the discontinuity of surface stress at a facet edge [16]. And growth kinetics can cause deviations from the equilibrium shape.

Our model can be easily extended to describe the nonwetting case. All that is needed is to generalize the surface energy term as $E_s = 2\Gamma_1 L_1 + 2\Gamma_2 L_2 - \Gamma_s(L_0 + 2L_1 + 2L_2)$, where $\Gamma_s = g_s - (g_0 + g_i)$, g_s is the surface energy of the (unwetted) substrate, and g_i is the interface energy. When $\Gamma_s < 0$ the deposited material does not wet the surface, but many features of the phase diagram remain the same. In the limit of infinitesimally negative
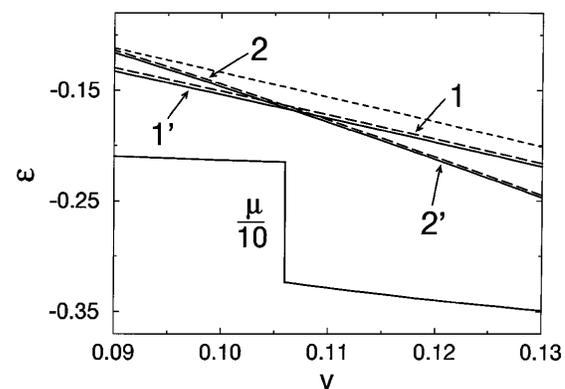

FIG. 4. Dimensionless island energy vs volume for $r = 0.2$ and $\Gamma_2 > 0$. Solid lines correspond to equilibrium islands (1' and 2'). Adjacent long-dashed lines represent islands constrained to have *no* top facet (1 and 2). Upper dashed line corresponds to saddle point energy; see text. The bottom solid curve represents the dimensionless chemical potential μ (divided by 10 to fit on graph). At the shape transition, μ is discontinuous, which radically affects growth and coarsening.

$\Gamma_s < 0$, the phase diagram is unaffected except for the elimination of the planar phase 0 in Fig. 3a. The 1'-2' and 2'-3' boundaries then extend to $\nu = 0$, nearly meeting there. For larger negative Γ_s, shallower facets (especially the top facet) shrink at the expense of steeper facets, reducing the island base area and increasing the height.

The shape transition has a profound effect on island growth. Normally the chemical potential of an island decreases continuously with size, due to the smaller surface/volume ratio. As a result, material diffuses from smaller to larger islands. In this coarsening or "Ostwald ripening," large islands grow while small islands shrink and disappear. The resulting time-dependent size distribution has been extensively studied [7]. It is unimodal, and not particularly narrow.

However, because the shape transition is first order, the energy-versus-volume curve has a discontinuous slope, as seen in Fig. 4. Thus the chemical potential is discontinuous. The dimensionless chemical potential $\mu = \partial \varepsilon(\nu)/\partial \nu$ is shown versus island volume in Fig. 4.

Ross *et al.* [11] showed that such a discontinuous chemical potential dramatically changes the coarsening behavior. (Those authors did not actually show that the chemical potential is discontinuous—rather, they considered a highly simplified model with a transition between two fixed pyramidal shapes, in which the transition can only be discontinuous.) When there are islands on both sides of the transition, there are much sharper differences of μ than in normal coarsening. This leads to an unusual bimodal size distribution [11]. Moreover, Ref. [11] showed that there is a transient regime where the islands have a narrow size distribution, peaked at a volume just above V_t. Here, we see here that the real equilibrium shape leads to a discontinuity in μ, validating the simplified model of Ref. [11].

Up to this point we have considered only the equilibrium shape, assuming that the shape transition occurs quickly compared to growth or coarsening. However, since the shape transition is first order, there is an energy barrier. If this barrier is too large, the transition might occur slowly or not at all on the experimental time scale.

We can calculate an upper bound for the energy barrier for the transition, by assuming that the island remains faceted during the transition. At ν_t, the island energy $\varepsilon(\nu, r, s, \lambda_1, \lambda_2)$ has two degenerate minima with respect to the shape (λ_1, λ_2). Even at somewhat larger or smaller volumes there remain two distinct minima. These are separated by a saddle point on the 2D energy surface defined by λ_1 and λ_2. The energy barrier to the shape transition is the energy of this saddle point, relative to the metastable shape (the higher of the two local minima). The saddle point energy is included in Fig. 4 (topmost line), and the resulting barrier is simply the difference between the saddle point energy and the next-lower solid line. However, it is not possible at present to calculate the barrier for specific real systems, because the required surface energy differences are not known even roughly.

In conclusion, the shape transition is predicted to be a very general phenomenon in island growth. It leads to a discontinuous change in chemical potential, which profoundly affects growth and coarsening of islands. Within a simple but reasonably realistic model, the phase diagram and phase transitions can be understood in detail, showing the unexpected richness of island growth.

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