Shape Transition in Growth of Strained Islands: Spontaneous Formation of Quantum Wires

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Strained epitaxial layers tend initially to grow as dislocation-free islands. Here we show that such islands, as they increase in size, may undergo a shape transition. Below a critical size, islands have a compact, symmetric shape. But at larger sizes, they adopt a long thin shape, which allows better elastic relaxation of the island's stress. We have observed such elongated islands, with aspect ratios greater than 50:1, in low energy electron microscopy studies of growth of Ag on Si(001). These islands represent a novel approach to the fabrication of "quantum wires."

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Strained epitaxial layers are inherently unstable; yet they can be grown, e.g., by molecular beam epitaxy, and are important in semiconductor devices. As a result, the relaxation of strain in such layers has long attracted intense interest [1–9]. Traditionally, the focus has been on formation of dislocations to relieve strain [1–3]. However, more recently it has been recognized that strained layers are *unstable* against shape changes [4–6], while they are *metastable* against formation of dislocations (which have a large activation energy for formation [10]). Shape changes such as island formation therefore constitute a major mechanism for strain relief.

Since uniform strained layers are unstable, during growth one would expect immediate formation of strained islands (plus perhaps an atomically thin wetting layer [11]) if kinetics permit, even at low coverage. This is precisely what was observed by Eaglesham and Cerullo [12], who identified the connection between island formation and strain relief for Ge on Si, independently of the layer-stability studies. Snyder *et al.* reached similar conclusions studying InGaAs on GaAs [13]. However, despite the recognized importance of island formation as a mechanism for strain relaxation without dislocations, only a few theoretical studies have been reported [7–9].

Here we derive an approximate expression for the energy of dislocation-free strained islands. With reasonable assumptions about the growth kinetics, we find a shape transition at a critical island size. Small islands have the expected compact shape, but at a critical size the symmetry of the island is broken. Larger islands become progressively elongated, quickly reaching a fixed asymptotic width. Thus these islands in effect constitute self-assembling quasi-one-dimensional "quantum wires."

We have observed the formation of such islands in growth of Ag on Si(001), using low energy electron microscopy (LEEM) [14]. The islands have widely varying lengths, but similar widths, as expected from the theory. Our results may shed light on other recent experiments [15–18] as well. In particular, we propose that the remarkable and puzzling island shapes observed by Mo *et al.* [15] for Ge on Si(001) reflect the same stress-induced behavior.

Previous studies of strained islands relied on numerical finite-element calculations [7,8]. In contrast, here we derive an explicit approximation for the energy, which provides a broad perspective on island behavior. For simplicity, we assume the island to be rectangular in shape, with width s, length t, and height h, in the x, y, and z directions, respectively. The edges are assumed to be beveled at an angle θ to the substrate, as illustrated in Fig. 1. While in general a real island may have a more complex shape, including rounding at higher temperature, the shape assumed here is sufficient to capture the important features such as size and aspect ratio.

For convenience we will refer to the substrate and island as Si and Ge (a classic strained-layer system), though our treatment is completely general. We take as our energy reference the Si substrate, plus a reservoir of Ge strained to match Si in the x and y directions, and free to relax in the z direction. Then the island energy can be written $E = E_s + E_r$, where E_s is the extra surface and interface energy, and E_r is the energy change due to elastic relaxation.

The extra surface energy is

$$E_s = st(\gamma_i + \gamma_t - \gamma_s) + 2(s+t) \times [h\gamma_e \csc\theta - h\cot\theta(\gamma_t + \gamma_s - \gamma_i)/2] , \quad (1)$$

where γ_s, γ_t, and γ_e are the surface energy (per unit area) of the substrate and of the island's top and edge facets, respectively, and γ_i is the island-substrate interface energy. The parameters s, t, h, and θ are defined in Fig. 1 and in the text above. We have omitted any terms

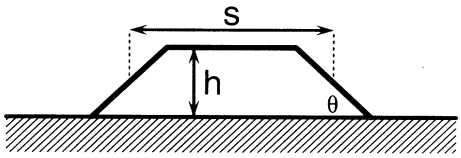

FIG. 1. Schematic of assumed crystal shape, showing cross section in xz plane, and illustrating definition of width s, height h, and contact angle θ.

corresponding to the corners.

For the case of coherent Stranski-Krastonow growth, where the strained material wets the surface before forming islands (as for Ge on Si [11,12]), the appropriate reference is not the bare substrate surface, but the wetted surface. In that case $\gamma_t = \gamma_s$ and $\gamma_i = 0$, so the surface energy term becomes

$$E_s = 2(s+t)h\Gamma , \tag{2}$$

where $\Gamma = \gamma_e \csc\theta - \gamma_s \cot\theta$.

An island under stress exerts a force on the surface, which elastically distorts the substrate. This lowers the energy of the island, at the cost of some strain in the substrate. To calculate this relaxation energy, we assume that the strain ε within the island does not vary in the z direction, i.e., $\varepsilon_{xz} = \varepsilon_{yz} = 0$. This is an excellent approximation if $s \gg h$ and $t \gg h$, and provides a variational upper bound on the relaxed energy in general. Then

$$E_r = -\frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}' \chi_{ij}(\mathbf{x}-\mathbf{x}') f_i(\mathbf{x}) f_j(\mathbf{x}') , \tag{3}$$

where $\mathbf{x}$ and $\mathbf{x}'$ are two-dimensional (2D) vectors, $f_i = \partial_j \sigma_{ij}$ is the force density at the surface, and χ is the elastic Green's function of the surface, which describes the linear response to an applied force. Here $\sigma_{ij} = \sigma_b \times h(\mathbf{x})\delta_{ij}$ is the 2D island stress tensor, σ_b is the xx or yy component of the bulk stress of Ge uniformly strained to the Si x and y lattice constants, and allowed to relax in z, and $h(\mathbf{x})$ is the height (thickness) of the island at position $\mathbf{x}$. We neglect the variation of σ as the island relaxes, a higher-order effect.

We solve (3) using the surface Green's function χ of an isotropic solid, and drop terms associated with the corners [19] (consistent with our neglect of corner terms in E_s), giving

$$E_r = -2ch^2 \left[s \ln\left(\frac{t}{\phi h}\right) + t \ln\left(\frac{s}{\phi h}\right) \right] . \tag{4}$$

Here $c = \sigma_b^2(1-\nu)/2\pi\mu$, and ν and μ are the Poisson ratio and shear modulus of the substrate. We write $\phi = e^{-3/2}\cot\theta$ for compactness. We have also expanded to second order in h/s and h/t, though we expect the results to be at least semiquantitatively correct even when this quantity is not small.

Combining Eqs. (2) and (4), the energy per unit volume of the island can be written

$$\frac{E}{V} = 2\Gamma(s^{-1}+t^{-1}) - 2ch\left[s^{-1}\ln\left(\frac{s}{\phi h}\right) + t^{-1}\ln\left(\frac{t}{\phi h}\right) \right] , \tag{5}$$

where $V = hst$ is the volume. [For the nonwetting case (Volmer-Weber growth), using the full Eq. (1) for E_s gives an additional term $h^{-1}(\gamma_i + \gamma_t - \gamma_s)$ in Eq. (5), and 2Γ becomes $2\gamma_e \csc\theta - (\gamma_t + \gamma_s - \gamma_i)\cot\theta$.]

Several approximations were made in deriving Eq. (5), including neglect of "corner" terms, and the variational assumption about the form of the strain. Even so, the result is exact in certain limiting cases where an analytic solution is already known [7], and should give an accurate picture of the overall behavior of strained islands. An explicit analytical form such as Eq. (5) is particularly valuable for identifying fundamental regimes of behavior for strained-layer growth. For example, besides the transition from symmetric to asymmetric islands discussed here, Eq. (5) can be used to calculate the size of the critical nucleus for coherent Stranski-Krastonow growth [20].

So far we have considered only the energetics, but island growth depends also upon the kinetics. We expect that, under a range of growth conditions, the kinetics are roughly as follows. As atoms arrive on the surface and diffuse to the island, they tend to stick to the beveled edge, and not to diffuse to the top facet of the island. As a result, the island height h grows slowly compared to s and t, and may be treated as roughly constant. (The effect of increasing island height will be addressed below.) This is especially true if diffusion is much more rapid on the substrate than on the island, e.g., because a high density of adatoms is being deposited.

We can incorporate these kinetics by minimizing the energy with respect to s and t, keeping h fixed. We shall assume for simplicity that θ is also fixed, being determined by the orientation dependence of the surface energy.

If we do not fix the total volume of the island, but instead minimize E/V with respect to s and t, we find $s = t = \alpha_0$, where

$$\alpha_0 = e\phi h e^{\Gamma/ch} . \tag{6}$$

Thus in the thermodynamic limit, where there are many islands (though far apart), the islands should "ripen," with the number of islands growing or shrinking until each island is a square of size α_0. This size represents the optimal tradeoff between surface energy and strain. The island edges permit elastic relaxation, as the cost of extra surface energy. If the surface energy Γ dominates, α_0 becomes very large to reduce the edge-to-area ratio. But if the island stress dominates ($ch \gg \Gamma$), then the minimum energy is obtained with many small islands.

This result may explain the peculiar behavior of Ag on Pt(111). Becker *et al.* [18] recently found that large monolayer islands of Ag could be grown at low temperature. However, when the system is annealed at high temperature, the large islands spontaneously fragment into much smaller islands. The same small monolayer islands develop if Ag is deposited at high temperature. We believe that elevated temperature, by increasing diffusion, simply permits the strained islands to attain their minimum-energy size α_0. (In addition, it is possible that thermal fluctuations could actually lower the free energy of the island edge, giving a smaller value of Γ and hence a

smaller value for α_0 at high temperature.)

However, under more typical growth conditions, the islands cannot maintain an optimal size. They are too far apart for "ripening" to take place on the relevant time scale. As additional material is added in the form of adatoms (e.g., from a molecular beam), at least some of the adatoms will diffuse to the nearest island, which will therefore grow beyond its optimal size.

We must therefore ask, what is the optimal *shape* of an island of a given size, assuming sufficient diffusion for the island to attain this shape? The answer can be obtained directly from Eq. (5). The resulting minimum-energy values of island width s and length t are shown in Fig. 2, versus total island area $A = st$. For island size $s = t < e\alpha_0$, the square island shape $s = t$ is stable. However, once the island grows beyond its optimal diameter α_0 by a factor of e, the square shape becomes unstable. There is a transition to a rectangular shape, as seen in Fig. 2(b). This transition is second order, i.e., the second derivative of the energy with respect to island size is discontinuous.

As the island grows, the aspect ratio t/s becomes ever larger. In the limit of large islands, the energy is minimized when s equals α_0 and $t = A/\alpha_0$. By achieving the optimal size in one direction, the island is guaranteed half its optimal relaxation energy; whereas if it grew large in both directions, the energy per unit area would go to zero.

We have actually observed such behavior, using LEEM to watch the growth of Ag islands on Si(001). Ag grows on Si(001) in an (001) orientation, but rotated 45°, giving a lattice mismatch of 6% [21]. Because of the cubic anisotropy of the substrate, the elongated islands are all oriented in one of two equivalent crystal directions, apparently at random. [The presence of Ag destroys or disorders the 2×1 reconstruction of Si(001), so the surface has fourfold rotational symmetry.] Similar behavior, though for less elongated islands, has also been seen by Hembree and Venables [17]. We assume that the islands are free of dislocations, as may be energetically preferred [7,9]. However, a partial relief of the stress would not affect the results here, beyond reducing the effective value of σ_b.

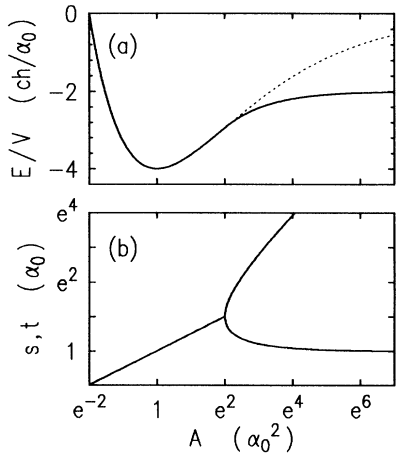

FIG. 2. (a) Energy per unit volume of island, in units of ch/α_0, vs island area A, assuming h and θ fixed. Dotted line shows energy if island remained square. (b) Width s and length t of island, vs A. Unit of length for s, t, and A is α_0 [see Eq. (6)]. Note logarithmic scale. For area less than $e\alpha_0 \times e\alpha_0$, s and t are equal, i.e., the island is square.

Unfortunately, we did not have the opportunity to monitor the entire growth sequence under fixed conditions. Nevertheless, we established that the Ag islands are initially compact, and become progressively elongated as they grow larger. Part of one large island is shown in Fig. 3. We have observed many such islands, including some with aspect ratios greater than 50:1. Though the lengths varied greatly between islands, all had similar widths. This otherwise inexplicable behavior constitutes compelling evidence that the island shape is controlled by the elastic strain-relief mechanism proposed here.

These islands provide a dramatic illustration of the importance of strain in island growth. But they may also have a more practical significance. Much effort has been devoted to studying quasi-one-dimensional structures, which act as "quantum wires" with fascinating electronic and optical properties [22]. However, it has proven extremely difficult to make long, straight wires of uniform width. The extravagantly elongated islands found here are in effect self-assembling quantum wires, and may point the way towards a new approach to the fabrication of such structures. While the islands here are metallic (Ag), there is evidence (discussed below) that similar behavior may be achievable for Ge on Si, and so presumably for other heteroepitaxial semiconductor systems as well.

So far we have treated the island height h as constant. However, while h may vary slowly compared with width s and length t, it will inevitably increase as the island

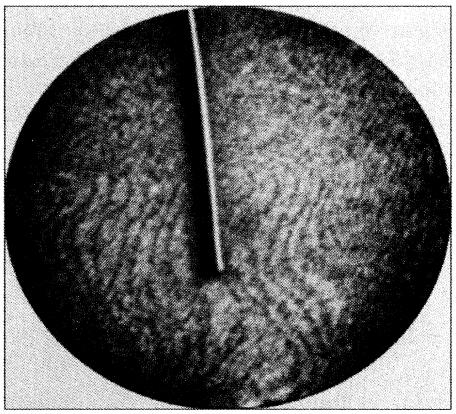

FIG. 3. Portion of a Ag island on Si(001), as seen with LEEM. Field of view is 6 μm. Faint wavy lines are steps on substrate surface.

grows, since this lowers the energy. As discussed above, the minimum-energy island width is $s=\alpha_0=e\phi he^{\Gamma/ch}$. This width decreases, relative to the height, with increasing h, until for $h \geq 2\Gamma/c$ the island becomes triangular in cross section. Thus as the island grows, not only does it become elongated, but it becomes triangular in cross section. This corresponds well with our observations. Small islands were clearly observed to have a (001) facet on top, while large islands appeared triangular or nearly triangular in cross section.

We emphasize that the central conclusions here do not depend on the approximations underlying Eq. (5). The transition from a compact to an elongated shape for a fixed-height island, and from a trapezoidal to a triangular cross section with increasing height, can be confirmed with just dimensional arguments. Including island-island interactions has only a slight effect, even at fairly high island densities [23]. Thus an *exact* calculation, if possible, would only shift the sizes at which these two transitions occur.

The behavior predicted here appears to give an excellent description not only of Ag on Si, but also of the initial growth of Ge on Si(001), as observed in great detail by Mo *et al.* [15]. Those observations have been a considerable mystery. Ge islands were found to be rectangular in plan view, with triangular cross sections in the short direction (the width). Most significantly, all islands had very similar widths, though the lengths varied greatly. The smallest islands were square, while the largest had aspect ratios of up to 8:1.

In fact, we believe that the formation of elongated islands should be common in strained-layer growth, since the assumptions made here for the kinetics seem widely applicable. At least two groups [16] have observed elongated GaAs islands on Si. (In that system, nucleation at steps may play an additional role [24].) Also, Mundschau *et al.* [25] observed elongated islands in growth of Au on Mo(111) and on Si(111), and Rousset *et al.* [26] observed elongated islands in growth of Au on Ag(110). When the stress is anisotropic, as in these latter cases, the island should align itself perpendicular to the direction of maximum stress. We expect that, with a clearer appreciation of the connection between strain and growth morphology, a variety of systems will be recognized as exhibiting the behavior proposed here.

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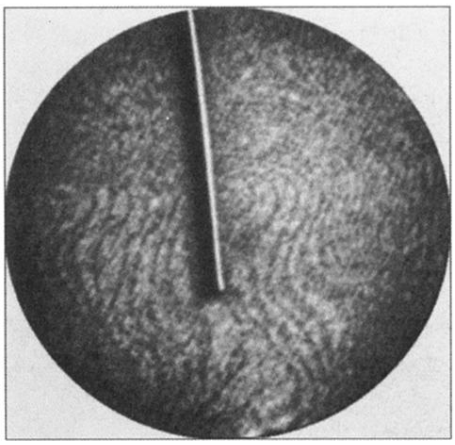

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