Morphological Evolution of Strained Films by Cooperative Nucleation

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We identify a new mechanism of stress driven surface morphological evolution in strained semiconductor films. Surface roughness forms by a cooperative mechanism involving the sequential nucleation of islands and pits, which is distinct from the conventional view of ripple formation as an Asaro-Tiller-Grinfeld (ATG) instability. This mechanism is operative both during annealing and growth and competes with the ATG instability as a kinetic pathway to ripple formation. [S0031-9007(96)00853-8]

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The morphological stability of stressed solids is a subject of considerable scientific and technological importance. It is directly relevant to several key issues in materials science ranging from stress corrosion cracking through to phase transformations and strained layer epitaxy. Since the pioneering work of Asaro and Tiller [1] and Grinfeld (ATG) [2], it is generally argued that above a critical wavelength λ_c the planar surface of a stressed solid is unstable to the formation of undulations [3–5]. This is because the energy reduction associated with elastic relaxation of the undulations exceeds the increase in surface energy. In the case of thin-film deposition, it is therefore envisioned that an initially planar film surface will gradually roughen in the growth direction over extended regions with a characteristic lateral wavelength. The observation of continuous surface ripple patterns on strained semiconductor layers over large areas would appear to give direct confirmation of this view [6,7]. Indeed, the patterns observed in cross section often closely resemble the sinusoidal roughness profiles used as a basis for the instability theory [8,9].

In this Letter we reveal an entirely new mechanism of surface ripple formation, which is linked to the activated nature of island and pit formation. The ripple forms by a cooperative mechanism involving the sequential nucleation of islands and pits. This is very different from the gradual strain induced roughening mechanism normally envisioned [3–9] and has important implications for our fundamental understanding of the 2D to 3D transition of strained systems.

To determine the mechanism of surface ripple formation we have studied the stress induced 2D to 3D transition in the technologically important $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ system. Our method involves a novel two stage process in which a thin (5 nm) planar $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ alloy layer is first grown at relatively low temperatures to ensure a nominally planar surface. The ripple morphology is then formed by a gentle postdeposition anneal at around 590 °C for 5 min. This approach emulates equilibrium surface conditions, at least locally, as closely as possible. A map of the surface evolution during growth was obtained from atomic force microscopy (AFM) measurements of the ripple geometry at different temperature regions of one sample wafer.

To capture the mechanism of surface ripple formation, use was made of the natural temperature gradient across the sample [10]. At the center of the wafer, corresponding to a temperature of 590 °C, a well-defined and continuous ripple geometry was observed using AFM as shown in Fig. 1(a). However, close to the edge region at 570 °C, isolated ripple domains consisting of alternating islands and pits were seen to be separated by planar regions of the strained layer [Fig. 1(b)]. This directly captures the transformation of a planar film to a ripple morphology. The continuous ripple in Fig. 1(a) is, therefore, just the coalesced stage of a cooperative nucleation process involving islands and pits. This is very different from the conventional ATG picture involving the simultaneous evolution of vertical roughness over large extended regions [3–9].

We now consider the physical origin of this cooperative nucleation mechanism of roughening. An isolated island (or pit) above a critical size will lower the energy of the planar strained film. However, to nucleate an island or pit it is first necessary to overcome an energy barrier [11]. Since the elastic interaction between islands and pits is negative (i.e., they attract), it is conceivable that cooperative effects may play an important role by lowering the activation barrier for domain growth. We therefore consider two possibilities of cooperative nucleation. The first possibility involves simultaneous nucleation in which an array of islands and pits form concurrently [12]. The second mechanism involves sequential nucleation where an island or pit nucleates adjacent to a preexisting stable configuration of islands and pits.

To examine these possibilities we consider a simple 2D model for domain growth which captures the essential physics of cooperative nucleation. Figure 2 shows several nucleation configurations involving various combinations of islands and pits. The nucleation of an individual island

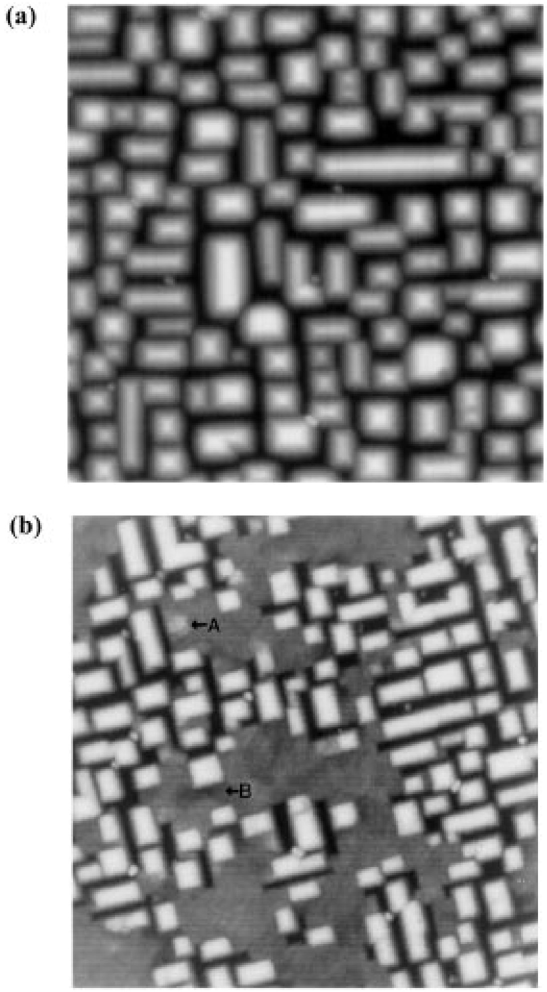

FIG. 1. AFM image of a 5 nm thick $Si_{0.5}Ge_{0.5}$ alloy layer grown on Si(001) and annealed for 5 min at 590 °C. (a) A regular surface ripple pattern is formed at the center of the wafer corresponding to an anneal temperature of 590 °C. (b) The cooperative nucleation of surface ripple domains is captured in the cooler edge region (570 °C). Islands (A) and pits (B) nucleate adjacent to each other as indicated, with substantial planar regions of the film remaining. The scanned area in both images is $1 \times 1\ \mu m^2$ and the typical height (depth) of islands (pits) is 2.5 nm in (a) and 5.0 nm in (b). Note that in both images, the islands and pits are bounded by {501} facets.

$(N = 1)$ of varying height h is, for simplicity, assumed to occur with a fixed width L. In the case of simultaneous nucleation (SM) the islands and pits of height and depth h form at the same time. In sequential nucleation (SQ) we consider the nucleation of an island (shaded) of varying height h adjacent to an existing stable set of islands and pits of height and depth A.

The energy change ΔG_N associated with the nucleation of these various configurations is the sum of the elastic relaxation energy and the additional cost in surface energy. The surface energy per unit length is simply the energy per unit area γ_f associated with the vertical island facets multiplied by the height of the islands or the depth of the pits. We evaluate the elastic relaxation energy noting that for each vertical facet, the discontinuity in the height of the surface creates a force monopole in the projected two-dimensional stress. The elastic relaxation energy can be obtained from the interaction of these monopoles so that for two facets a distance L apart the interaction energy is $C_m \sigma^2 h_1 h_2 \ln(L/a)$ [13]. Here, h_1 and h_2 are the facet heights, σ is the misfit stress, and C_m is an elastic constant. The microscopic cutoff length a is usually taken as a lattice constant. The interaction is positive (attractive) if the facets are the same sense (e.g., both down facets) or negative (repulsive) for opposite sense facets (e.g., up and down facets).

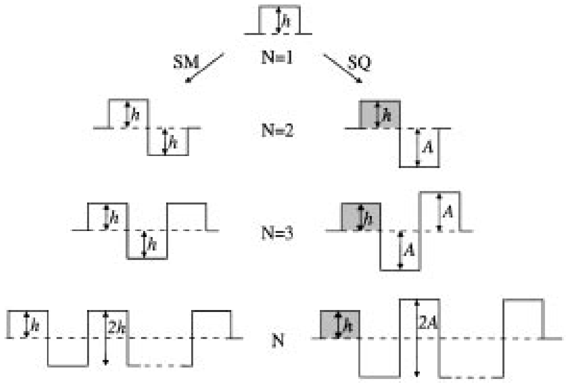

FIG. 2. Cooperative nucleation mechanisms in strained layer epitaxy. Various configurations are shown in the cross section corresponding to the simultaneous (SM) or sequential (SQ) nucleation of N islands and pits. In the case of simultaneous nucleation, the islands (pits) of height (depth) h all grow concurrently. For sequential nucleation, an island of height h (shaded) nucleates next to an existing arrangement of islands and pits of height (depth) A.

The energy change ΔG_1 associated with the nucleation of an isolated island is displayed in Fig. 3(a). Clearly, to attain a stable geometry, the island must first overcome in activation barrier ΔG_1^* which occurs at a height h^*. The energy barrier ΔG_N^* associated with the simultaneous or sequential nucleation of N pits and islands is displayed in Fig. 3(b). For SM, the activation barrier increases linearly with N. Since the nucleation rate of a domain is proportional to $\exp(-\Delta G_N^*/kT)$, the collective nucleation of a domain consisting of N pits and islands is far less probable than the nucleation of an individual island. Conversely, the activation barrier for the SQ of a pit adjacent to an existing stable island decreases relative to ΔG_1^*. Furthermore, the reduced energy barrier is approximately constant if the island nucleates adjacent to domains of several pits and island. This result strongly suggests that after the first nucleation event involving an individual pit or island, the domain will rapidly grow laterally with a reduced activation barrier via the sequential nucleation of islands and pits, as observed experimentally in Fig. 1(b).

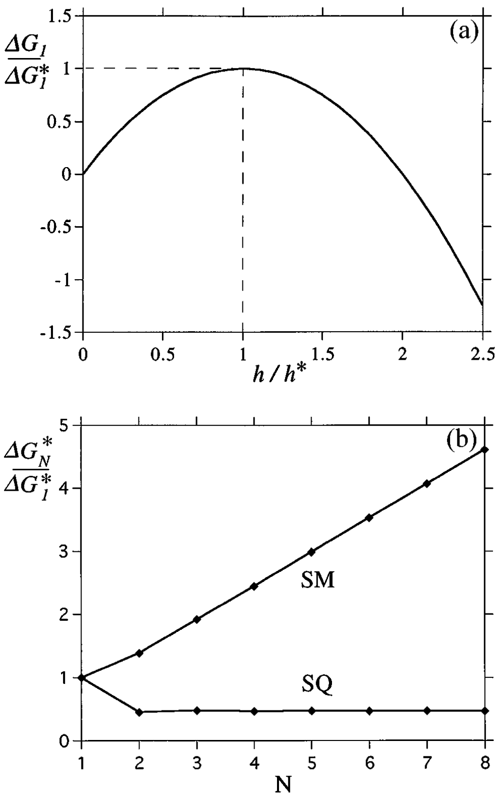

FIG. 3. (a) Energy ΔG_1 for the nucleation of the 2D island ($N = 1$) shown in Fig. 2 as a function of height h. To attain a stable geometry the island must first overcome the energy barrier ΔG_1^*, which occurs at height h^*. (b) Energy barrier ΔG_N^* associated with the simultaneous (SM) or sequential (SQ) nucleation of N islands and pits as displayed in Fig. 2. We assume $L = 45$ nm, $A = 2.5$ nm, $a = 2$ Å. $\gamma_f = 1.0\ \mathrm{J\,m^{-2}}$, with a shear modulus $\mu = 40\ \mathrm{GN\,m^{-2}}$ and Poisson's ratio $v = 0.3$ in the elastic constant $C_m = (1 - v)/\pi\mu$. The misfit $\varepsilon = 0.02$.

The reason why sequential nucleation is favored over simultaneous nucleation can be understood as follows. Simultaneous nucleation, although involving a beneficial elastic interaction between pits and islands, also requires a proportionate increase in surface energy which dominates in the nucleation process and raises ΔG_N^*. In the case of sequential nucleation, a fresh island gains all of the elastic interaction energy while only costing its own surface energy which lowers the barrier. Note that these basic arguments concerning sequential and simultaneous nucleation appear to be quite general and independent of the detailed geometry and parameterization of our model for domain growth.

It now remains to determine the conditions for which this cooperative mechanism for surface ripple formation is important. The mechanism relies on the elastic interaction between islands and pits. However, like an island, a pit must also grow beyond a critical nucleus size to become stable [11]. For a pyramidal pit, this defines a minimum film thickness h_p for pit formation

$$h_p = \frac{8\Gamma}{9C_m\sigma^2}, \tag{1}$$

where $\Gamma = \gamma_0 \csc\theta - \gamma_s \cot\theta$ with γ_θ the facet energy inclined at angle θ and γ_s the planar surface energy. Below h_p, only islands are accessible as a means of strain relaxation [14]. This is in agreement with results obtained by annealing a 2 nm thick planar $Si_{0.5}Ge_{0.5}$ layer in which only islands were observed [15].

Annealing experiments can be regarded as an extremum in the phase space of growth parameters since a quenched planar strained layer represents a highly nonequilibrium state. During deposition, we would expect the nucleation mechanism of rippling to be important whenever the kinetic barriers for island or pit formation are reasonable on the scale of the available thermal energy. Indeed, this might directly explain the observations of Cullis *et al.* [16] for the deposition of $In_{0.25}Ga_{0.75}As$ on GaAs(001) where the ripple also appears to be forming from ordered but discontinuous ripple arrays.

For high misfit systems, coherent islands will form almost immediately after deposition of a wetting layer [17–20] since ΔG_1^* depends on σ^{-4} [11]. Under such circumstances, the energy barrier for island nucleation is relatively small so that islands already provide an efficient means of strain relaxation before the critical film thickness for pit formation is reached [Eq. (1)]. Lower misfit systems will, on the other hand, prefer to roughen more gradually through stress driven surface diffusion as the energy barriers for island or pit nucleation become insurmountable [21].

In summary, we have revealed a new mechanism of surface ripple formation in strained layer epitaxy which has important implications for our fundamental understanding of the strain induced 2D to 3D transition. The mechanism is based on the sequential nucleation of islands and pits, which is very different from the conventional view of ripple formation as an instability [3–8]. We believe that the central idea of strain relief through sequential nucleation is quite general and could provide a useful means for fabricating novel surface morphologies with possible applications in nanotechnology.

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