Role of Strain-Dependent Surface Energies in Ge/Si(100) Island Formation

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Formation energies for Ge/Si(100) pyramidal islands are computed combining continuum calculations of strain energy with first-principles-computed strain-dependent surface energies. The strain dependence of surface energy is critically impacted by the presence of strain-induced changes in the Ge {100} surface reconstruction. The appreciable strain dependencies of rebonded-step {105} and dimer-vacancy-line-reconstructed {100} surface energies are estimated to give rise to a significant reduction in the surface contribution to island formation energies.

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The Stranksi-Krastanov (SK) mode of thin-film growth continues to receive widespread interest as a framework for the self-assembly of nanometer-scale "quantum dot" islands. Over the past decade extensive experimental and theoretical research has been aimed at elucidating the dominant kinetic and thermodynamic factors governing island formation in SK growth. In the traditional picture, relaxation of elastic energy provides the underlying driving force for island formation in an epitaxially strained thin film. This driving force competes with a surface-energy cost that is expected to rise with the increasing surface area accompanying island formation. There results a critical size for island formation governed by the relative magnitudes of these competing bulk and surface-energy contributions. The picture becomes considerably more complex when one considers that surface energy is itself intrinsically strain dependent (e.g., [1,2]). For example, it has been shown by Shchukin *et al.* [1] that for certain choices of surface stress it is possible for the net surface-related contribution to the island formation energy to be *negative*. While strain dependencies of surface energy (i.e., surface stresses) have been demonstrated to be potentially critical factors underlying the thermodynamics of SK growth, relatively small effects associated with surface stress were obtained in the most quantitative, system-specific calculations of island formation energies, performed for InAs/GaAs [3].

In this Letter, we investigate the effects of strain-dependent surface energies on the formation energies of isolated {105} pyramidal ("hut") islands in Ge/Si(100) [4]. We employ a hybrid computational approach (e.g., [3]) combining continuum calculations of strain energy with first-principles results for {100} and {105} [5] surface energies. The strain dependence of surface energy is critically impacted by the presence of strain-induced changes in the Ge {100} surface reconstruction. Relative to island formation energies calculated employing surface energies for a stress-free Ge crystal (i.e., neglecting surface stress) the net effect of strain-dependent surface energies is shown to be a sizeable *reduction* in the surface contribution to the island formation energy. For island sizes in the range of 10 nm, the magnitude of this surface-energy correction is found to be comparable to the elastic relaxation energy and is therefore an important factor stabilizing island formation.

We consider an isolated {105} Ge square-based pyramid atop a Ge wetting layer (WL) on a Si (100) substrate (see Fig. 1) and make use of the following decomposition of the island formation energy:

$$\Delta E^{\text{form}} = \Delta E^{\text{relax}} + \Delta E^{\text{surf}} + \Delta E^{\text{edge}}. \quad (1)$$

ΔE^{form} is the difference in energy between the system with an island and an equivalent amount of Ge in a planar epitaxial film. ΔE^{relax} is the difference in elastic strain energy, ΔE^{surf} is the net change in surface energy accompanying island formation, and ΔE^{edge} is the contribution from edges at the pyramid base and sides. In evaluating ΔE^{surf} we explicitly account for strain-dependent surface energies [6]:

$$\Delta E^{\text{surf}} = \int_{100} [\gamma_{100}(\epsilon_{ij}) - \gamma_{100}(\epsilon_0)] ds + \int_{105} [\gamma_{105}(\epsilon_{ij}) - \gamma_{100}(\epsilon_0)\cos(\alpha)] ds, \quad (2)$$

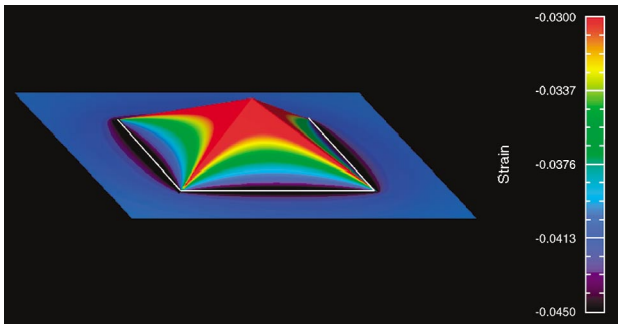

FIG. 1 (color). Isolated {105} pyramidal hut island on Si(100), colored according to one-half the trace of the calculated *in-plane* surface strain fields (see text for discussion).

where the integrals extend over the surfaces of the (100) WL film outside the pyramid and the {105} pyramid facets, respectively. In the second integral, α is the angle between (100) and (105) planes, and $\cos(\alpha)$ accounts for the (100) projection of the pyramid-facet surface area. $\gamma_{100}(\epsilon_{ij})$ and $\gamma_{105}(\epsilon_{ij})$ are the strain-dependent Ge surface energies for {100} and {105} orientations, and $\epsilon_0 \equiv -0.042$ denotes the misfit strain for a flat Ge epitaxial film on Si(100).

To calculate the strain fields and elastic relaxation energy arising from island formation, we employ isotropic elasticity theory using the small-slope approximation [10–12], neglecting differences between the elastic constants of the substrate and thin film (we used elastic-moduli values for Ge). Calculated surface strain fields are plotted in Fig. 1 for an isolated Ge {105} pyramid. Colors denote contours for $\frac{1}{2}$ the trace of the surface strain tensor, with blue corresponding to the misfit strain ϵ_0, and red and black areas indicating regions of strain, respectively, less compressive than $\epsilon = -0.03$ and more compressive than ϵ_0. An important feature of these results, observed previously (e.g., [3]), is the ring of enhanced compressive strain at the base of the island.

To compute ΔE^{surf}, we make use of the first-principles calculated values for the Ge {100} and {105} surface energies, plotted as a function of biaxial strain ($\epsilon_{\text{biaxial}}$) in Fig. 2. The {100} results were computed in this work for tilted-dimer $p(2 \times 2)$ and $p(2 \times 2)$-based 2×6 and 2×8 dimer vacancy line (DVL) reconstructions (e.g., [13]). We used the *ab initio* program VASP [14,15], employing ultrasoft pseudopotentials (USPP) [15] and the Perdew-Zunger [16] parametrization of the exchange-correlation energy within the local-density approximation (LDA). The {105} results are taken from recent comparable VASP-USPP-LDA calculations by Migas *et al.* [5] of the rebonded-step (RS) reconstruction [17–19]. Further calculation details are given below [20].

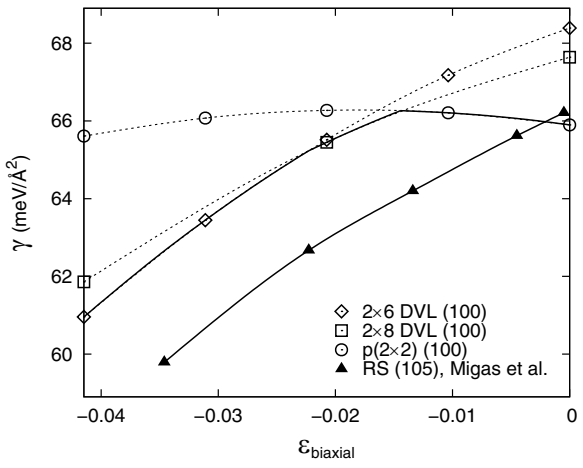

FIG. 2. Ge (100) and (105) surface energies (per unit area of deformed surface) versus biaxial strain. Triangles denote (105) results from Ref. [5]. Circles, squares, and diamonds are (100) results obtained in this work for $p(2 \times 2)$ and $p(2 \times 2)$ based 2×6 and 2×8 DVL reconstructions, respectively. Solid lines highlight the surface energy for the stable reconstruction of a given orientation.

In Fig. 2 the calculated {100} and {105} surface energies at $\epsilon_{\text{biaxial}} = 0$ (corresponding to stress-free bulk Ge) are nearly equal. With increasing compressive strain, γ_{105} decreases monotonically with a slope of ~ 210 meV/Å^2. Similar results for γ_{105} were recently obtained from generalized-gradient-approximation first-principles calculations by Hashimoto *et al.* [21]. The {100} surface energy displays a more complex strain dependence. For small compressive strains the $p(2 \times 2)$ reconstruction has the lowest calculated surface energy. When $\epsilon_{\text{biaxial}} \approx -0.015$, the surface undergoes a strain-induced structural transition with the $p(2 \times 2)$-based 2×8 DVL reconstruction becoming stable. A second strain-induced transition occurs at $\epsilon_{\text{biaxial}} \approx -0.022$, beyond which the 2×6 DVL reconstruction is stable. The strain-induced stabilization of the DVL reconstructions found here is consistent with previous theoretical modeling which emphasizes the importance of the tensile stress in the rebonded atoms beneath the DVLs [22,23]. The relief of this local tensile stress with increasing compressive strain stabilizes the DVL reconstructions, which are unstable for a stress-free Ge surface. In contrast to the $p(2 \times 2)$ surface, the DVL-reconstructed

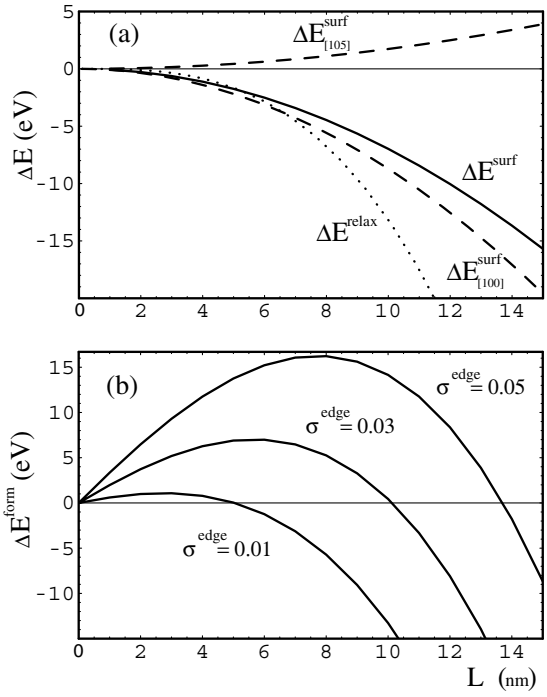

FIG. 3. Contributions to the formation energy of an isolated Ge {105} pyramidal island versus size (L). (a) ΔE^{relax} (dotted lines) and ΔE^{surf} (solid line) along with the {100} and {105} contributions to ΔE^{surf} (dashed lines); (b) ΔE^{form} for various edge energies, σ^{edge}, in eV/Å.

Ge (100) surface energy increases with a slope of magnitude similar to that for RS {105} ($\sim$180 meV/Å^2).

At $\epsilon_{\text{biaxial}}$ in the range of the Ge/Si misfit ($\epsilon_{\text{biaxial}} \approx \epsilon_0$) γ_{105} is lower than γ_{100}. In fact, since γ_{100} is larger than $\sqrt{26/25} \times \gamma_{105}$, our results predict that Ge {100} surfaces under compressive biaxial strains near ϵ_0 are unstable with respect to {105} faceting. We emphasize, however, that the difference in calculated surface energies is very small: $\delta \equiv \sqrt{26/25} \times \gamma_{105} - \gamma_{100} = -1.3$ meV/Å^2, or $\sim$20 meV per (100) surface atom. Since δ is within the estimated precision of the calculated {100} and {105} surface-energy differences [20], further calculations are required to confirm this prediction. To address the issue of {105} microfaceting more definitively, such calculations should consider the higher-order $M \times N$ {100} reconstructions [13] and the role of entropic contributions to the surface free energy. For the present analysis, we emphasize two main features of the results in Fig. 2: the calculated surface energies for {100} and {105} orientations are very close, and both γ_{100} and γ_{105} show comparable and appreciable strain dependencies near ϵ_0.

Figure 3(a) compares, as a function of island size, the calculated total surface-energy (solid line) and elastic relaxation (dotted line) contributions to the island formation energy. Island size is denoted by the length L of the pyramid base. The terms $\Delta E^{\text{surf}}_{[100]}$ and $\Delta E^{\text{surf}}_{[105]}$ (dashed lines) are the first and second terms on the right-hand side of Eq. (2), respectively. In evaluating these contributions we make use of a linear approximation and a polynomial fit for the dependence of γ_{100} and γ_{105}, respectively, on strain near ϵ_0. Because of the symmetry of the surface strain fields surrounding a square-based pyramid, and the 45° orientation of the pyramid edges to the dimer bonds on the (100) surface, $\Delta E^{\text{surf}}_{[100]}$ can be written as an integral of the product of the trace of the surface-stress tensor times the trace of the surface strain; i.e., the magnitude of $\Delta E^{\text{surf}}_{[100]}$ is independent of the anisotropy of the surface stress. While this is not the case for $\Delta E^{\text{surf}}_{[105]}$, we nevertheless are forced to make use of an isotropic approximation since only the trace of the surface-stress tensor can be derived from published calculations [5,21].

The term $\Delta E^{\text{surf}}_{[100]}$, associated with the WL film *surrounding* the island, is zero by definition for strain-independent γ_{100} [see Eq. (2)] and is negative in Fig. 3(a). For $L \approx$ 10 nm, representing the lower range of sizes where fully developed pyramid islands are observed experimentally in Ge/Si(100) (e.g., [24]), $\Delta E^{\text{surf}}_{[100]}$ has a magnitude comparable to ΔE^{relax}. The magnitude and sign of $\Delta E^{\text{surf}}_{[100]}$ arise from the tensile nature of the surface stress for {100} DVL-reconstructed Ge surfaces combined with the enhanced compressive strain in the WL film near the pyramid base resulting from island relaxation. By contrast, $\Delta E^{\text{surf}}_{[105]}$ is weakly positive, reflecting the competing contributions of (i) the substitution of (105) surface for (100) surface (negative contribution associated with the surface-energy difference term δ, discussed above) and (ii) the tensile Ge {105} surface stress combined with the less compressive strain on the pyramid facets resulting from island relaxation (positive contribution). The net surface contribution to the island formation energy, $\Delta E^{\text{surf}} = \Delta E^{\text{surf}}_{[100]} + \Delta E^{\text{surf}}_{[105]}$, is negative. The results in Fig. 3(a) demonstrate an important island-stabilizing effect associated with strain dependencies of surface energy. Specifically, if one evaluates ΔE^{surf} for a 10 nm pyramid using γ_{105} and γ_{100} for a stress-free Ge crystal ($\epsilon = 0$, neglecting surface stress), a value of $\Delta E^{\text{surf}} \equiv \Delta E^{\text{surf}}_0 = 18$ eV is obtained, which is 25 eV higher than the value of -7 eV calculated here.

To further analyze the role of strain-dependent surface energies, particularly in light of the separation of $\Delta E^{\text{surf}}_{[105]}$ into contributions (i) and (ii) above, we rewrite ΔE^{surf} as

$$\Delta E^{\text{surf}} = \Delta E^{\text{surf}}_0 + \Delta E^{\text{surf}}_{\text{hom}} + \Delta E^{\text{surf}}_{\text{het}}, \tag{3}$$

where ΔE^{surf}_0 is, as defined above, derived for surface energies at $\epsilon = 0$, neglecting surface stress. $\Delta E^{\text{surf}}_{\text{hom}}$ is associated with the change in γ_{100} and γ_{105} when the Ge surface is *homogeneously* and biaxially strained to the misfit strain (ϵ_0). $\Delta E^{\text{surf}}_{\text{het}}$ results from the heterogeneous strain field induced by island relaxation. Writing ΔE^{surf} as in Eq. (3) also allows us to make direct contact with the analysis presented in the earlier work of Shchukin *et al.* [1]. Note that, in the absence of γ strain dependencies, both $\Delta E^{\text{surf}}_{\text{hom}}$ and $\Delta E^{\text{surf}}_{\text{het}}$ are identically zero. Furthermore, in a model employing strain-independent surface energies derived where $\epsilon = \epsilon_0$, $\Delta E^{\text{surf}}_{\text{het}}$ is zero.

Considering first the term $\Delta E^{\text{surf}}_{\text{hom}}$, in the work of Shchukin *et al.* it was assumed that *surface stresses* for the film (τ_{100}) and island facets (τ_{105}) are strain independent (implicitly derived at $\epsilon = 0$). In this case, one can write $\Delta E^{\text{surf}}_{\text{hom}} = [\tau_{105}/\cos(\alpha) - \tau_{100}]\epsilon_0 L^2$. This simple form is insufficient for Ge/Si(100) due to the strain-induced changes in the {100} surface reconstructions (see Fig. 2). More generally, we may write $\Delta E^{\text{surf}}_{\text{hom}} = [\delta\gamma_{105}/\cos(\alpha) - \delta\gamma_{100}]L^2$, where $\delta\gamma_{105} = [\gamma_{105}(\epsilon = \epsilon_0) - \gamma_{105}(\epsilon = 0)]$, and similarly for $\delta\gamma_{100}$. From this more general definition our results yield $\Delta E^{\text{surf}}_{\text{hom}} = -41$ eV for a 10 nm pyramid.

$\Delta E^{\text{surf}}_{\text{het}}$ is defined as the change in net surface energy resulting from heterogeneous strain fields generated by island relaxation. This term includes a negative contribution from the (100) WL surface, equal to $\Delta E^{\text{surf}}_{[100]}$, and a positive contribution from $\Delta E^{\text{surf}}_{[105]}$ [specifically, part (ii) described above]. Due in part to a Poisson-type expansion of the island normal to the WL surface, for this system and island geometry we obtain a net positive value of $\Delta E^{\text{surf}}_{\text{het}} =$ 16 eV for a 10 nm pyramid.

We thus find that both $\Delta E^{\text{surf}}_{\text{hom}}$ and $\Delta E^{\text{surf}}_{\text{het}}$ are of appreciable magnitude and provide a net negative contribution to ΔE^{surf} of -25 eV for a 10 nm pyramid. This contribution, representing the effect of strain-dependent surface energies

on island formation, when added to ΔE_0^{surf} yields $\Delta E^{\text{surf}} = -7$ eV, as plotted in Fig. 3(a). Note that the magnitudes of $\Delta E_{\text{hom}}^{\text{surf}}$ and $\Delta E_{\text{het}}^{\text{surf}}$ are determined primarily by the relative magnitudes of the surface stresses for the {105} and DVL-reconstructed {100} Ge surfaces, and are unaffected by uncertainties in the first-principles calculations which would give rise to a uniform shift of γ_{105} relative to γ_{100}.

The first two terms on the right side of Eq. (1) are noted to be negative for all L. In Fig. 3(b) it is demonstrated that the introduction of relatively modest (isotropic and strain-independent) values for the edge energies (σ) [25] gives rise to a maximum in ΔE^{form} at nanometer-scale critical sizes, below which islands are thermodynamically unstable and above which they are stable.

Employing a hybrid computational approach, we have conducted a comprehensive analysis of the formation energetics of isolated Ge pyramid islands on Si(100), including strain-dependent Ge {100} and {105} surface energies. The strain dependence of γ_{100} is critically dependent on the Ge {100} surface reconstruction, which undergoes a sequence of strain-induced structural transitions. Strain dependencies of γ_{100} and γ_{105} give rise to a sizeable reduction in the surface-energy contribution to island formation energies, of a magnitude that is larger than the calculated elastic relaxation energy for a representative island size of 10 nm. These results highlight the delicate and subtle balance between surface, bulk, and edge energies controlling the formation of pyramid islands in Ge on Si(100).

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[6] We consider the limiting case where island formation does not modify the height of the WL film outside the island, taken as the critical thickness of ~3 ML (monolayers). The excess energy of the WL, Γ_{WL}, is modeled as the sum of γ_{100}^{Ge}, the Ge/Si interface energy, and an interface/surface interaction underlying the thickness dependence of Γ_{WL} (e.g., [7]). Island formation modifies Γ_{WL} through the strain dependence of these terms and the change in the interface/surface interaction for regions of varying height covered by the island. Equations (1) and (2) are justified assuming (i) the interaction energy is small beyond the critical WL thickness, and (ii) strain dependencies of the interface and interaction energies are negligible. Island formation thus modifies Γ_{WL} only through the strain dependence of γ_{100}^{Ge}, i.e., giving the first term in Eq. (2). Previous calculations [7–9] support the first assumption. In support of the second, we have computed the strain dependence of Γ_{WL} for a 3 ML thick Ge film on Si (001). The calculated strain dependence agrees to within a few percent of that for a pure Ge (100) surface.
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[20] Our calculations employed a plane wave cutoff of 174 eV and slab supercells with ≥25 Å vacuum between slabs and 13 relaxing layers for each surface of interest. Reciprocal-space summations employed k-point meshes with densities equivalent to 8×8 k points per surface unit cell for the $p(2 \times 2)$ and 2×8 DVL reconstructions, and 8×12 k points for the 2×6 DVL structure. Perpendicular to the surface a single k point was employed for supercells with periodic heights of 10 bulk lattice constants. From convergence tests of computed surface energies with respect to k-point density, plane wave cutoff and slab and vacuum thickness absolute convergence of γ_{100} is estimated at ~1 meV/Å^2. In the Migas *et al.*, calculation of γ_{105} [5] the same pseudopotentials and exchange correlation were used, with slightly higher k-point densities and plane wave cutoff (200 eV). Their $p(2 \times 2)$ surface energies agree with ours to within 0.5 meV/Å^2. A quantitative estimate of absolute convergence was not given in Ref. [5]; assuming a similar level of convergence to that in the present calculations, the precision of the difference $\gamma_{100} - \gamma_{105}$ is estimated as ~1–2 meV/Å^2.
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