Towards Quantitative Understanding of Formation and Stability of Ge Hut Islands on Si(001)

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We analyze Ge hut island formation on Si(001), using first-principles calculations of energies, stresses, and their strain dependence of Ge/Si(105) and Ge/Si(001) surfaces combined with continuum modeling. We give a quantitative assessment on strain stabilization of Ge(105) facets, estimate the critical size for hut nucleation or formation, and evaluate the magnitude of surface stress discontinuity at the island's edge and its effect on island stability.

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Since its discovery a decade ago [1], the formation of the (105)-faceted Ge and SiGe ''hut'' (pyramidal island) on Si(001) has attracted much interest, both because it serves as an ideal model system for studying heteroepitaxial growth of thin films, in particular, self-assembly of strained islands [2], and because it has a potential technological application as quantum dots. Although much progress has been made [3–14], our understanding is still far from complete.

So far, theoretical studies [3,4,11] have focused on a qualitative understanding of hut formation, due to the lack of quantitative information. The formation of strained islands is generally driven by the relaxation of strain energy at the expense of increase of surface energy. The special feature of the hut is that it is bounded by (105) facets that form above the Ge wetting layer on Si(001). Thus, it will be very useful to be able to compare the energies between the Ge/Si(105) and Ge/Si(001) surfaces and to evaluate their strain dependence to better understand the physical origin of (105) faceting. The surface energies may further be used as input parameters for continuum modeling to estimate the ''critical'' size for hut nucleation or formation.

In addition, surface stress tensors of Ge/Si(105) and Ge/Si(001) are useful quantities in helping understand hut stability. Continuum models show that if only the strain relaxation energy (proportional to island volume) and the surface energy (proportional to island surface area) are present, there will be no stable island size [3]. However, if surface stress of the island facet and of the wetting layer is different, there is an additional elastic edge relaxation energy that may induce a stable island size against coarsening [4]. So far, no quantitative evaluation has been made on the significance of such edge stress relaxation energy on Ge hut stability.

Here, we perform first-principles calculations of surface energies, surface stresses, and their strain dependence of Ge/Si(105) and Ge/Si(001) and combine them with continuum modeling, to quantitatively analyze the formation and stability of Ge huts on Si(001). We show that the surface energy of Ge(105) after being compressively strained onto Si(105) is 61.4 meV/Å^2 (1 meV/Å^2 = 0.016 J/m^2), which happens to be very close to that of the strained Ge(001) surface on Si(001) of 3- to 5-layers thick (62.5–60.7 meV/Å^2). The Ge(105) facet is stabilized by the (2×1)-rebonded step (RS) reconstruction [15,16] that reduces the number of dangling bonds from 20 to 8 and by the compressive strain that relieves the large tensile surface stress associated with the (2×1)-RS reconstruction. We estimate the critical size for nucleation is ~110–160 Å (base size) for a pure Ge pyramidal hut, and it increases for SiGe alloy huts, in good agreement with experiments [3–14]. Furthermore, we evaluate the magnitude of surface stress discontinuity at the island edge and show its effect to be too small to induce a stable size for the Ge hut.

Our calculations are performed using the pseudopotential plane wave total-energy method and the supercell slab technique, as used before for other Si and Ge surfaces [17]. We note that it is until very recently that the correct reconstruction of the strained Ge(105) surface has been determined [15,16], making these calculations feasible. Figure 1 shows the calculated surface energies of Ge/Si(105) and Ge/Si(001) as a function of the number of deposited Ge layers. For comparison, we renormalized the Ge(105) layer number into (001) corresponding to the

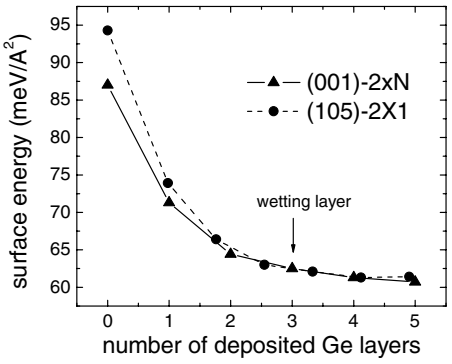

FIG. 1. Surface energies of Ge/Si(105) and Ge/Si(001) as a function of the number of deposited Ge layers.

same film thickness, as every ~2.55 (105) layers corresponds to one (001) layer. For Ge/Si(105) surfaces, the (2×1)-RS reconstruction [15,16] was used. For Ge/Si(001) surfaces, the $p(2 \times 2)$ was used for Si(001), and the $(2 \times N)$ reconstruction [17,18] was used with $N = 10$ for 1 layer of Ge and $N = 8$ for 2 to 5 layers of Ge, all optimized to be the most stable surface.

The surface energy of Si(105) is 94.2 meV/Å^2, noticeably higher than that of Si(001), 87.1 meV/Å^2. Upon Ge deposition, they both decrease but the Ge/Si(105) energy decreases faster; at about 3 layers of Ge deposition, the two surface energies become almost degenerate, as shown in Fig. 1. This indicates quantitatively that, in comparison to the (001) surface, the Si(105) surface is unstable but the Ge/Si(105) surface becomes stable so that huts are bounded by (105) facets. This is consistent with the experimental observation that a clean Si(105) surface has a very rough morphology [15] but becomes smooth upon Ge deposition as a stable facet [5,15]. Also, the number of Ge layers needed for the energy of the Ge/Si(105) surface to become comparable to that of the Ge/Si(001) surface corresponds well to the critical Ge wetting-layer thickness for hut formation [1,18].

Our calculations show that the (2×1)-RS reconstruction lowers the Si(105) surface energy from 103.5 meV/Å^2 of the bulk-terminated (1×1) surface to 94.2 meV/Å^2 of the reconstructed surface by reducing the number of dangling bonds from 20 to 8 but introducing a large tensile surface stress [192.4 meV/Å^2, increased from 84.2 meV/Å^2 in the (1×1) surface], rendering its instability. The role of Ge deposition is to relieve the tensile surface stress by applying a compressive strain and hence to stabilize the surface. Figure 2 shows the average surface stresses of Ge/Si(105) and (001) surfaces, illustrating the quantitative stress reduction. The Ge film is under ~4% compression. The surface stress applied by the compressed Ge film equals its bulk stress times the film thickness. Consequently, deposition of Ge should drive the surface toward compression linearly. This is confirmed in Fig. 2 where surface stress decreases linearly beyond 2 layers of Ge deposition after the surface structure converges. The surface stress of Ge/Si(001) displays the same trend as Ge/Si(105) with lower values.

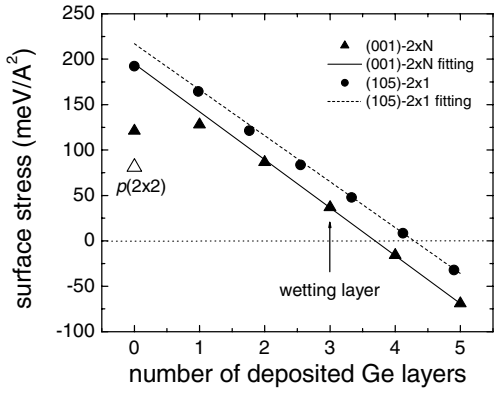

FIG. 2. Average surface stresses $(\sigma_{xx} + \sigma_{yy})/2$ of Ge/Si(105) (circles) and Ge/Si(001) (triangles) as a function of the number of deposited Ge layers. Positive means tensile; negative means compressive. Lines are linear fits to the 3 high-coverage data points.

Thus, it becomes clear that the Ge(105) facet on huts is partly stabilized by the compressive strain relieving the large tensile stress associated with the (2×1)-RS reconstruction [15]. This is also supported by calculations of a pure Ge(105) surface [not on the Si(105) surface], which show that the unstained Ge (105) surface has an energy of 66.0 meV/Å^2 and a large tensile stress of 154.9 meV/Å^2, while the energy of the Ge(105) surface strained to the Si lattice constant is lowered by ~8 to 58.5 meV/Å^2 [19] with a stress decreasing toward compression linearly with increasing film thickness.

Next, we use the first-principles surface energies to estimate the critical size for hut nucleation or formation. We consider the hut having a square-based pyramidal shape [1,6–9], with height h, base l, and contact angle $\theta \sim 11.3°$, as shown in Fig. 3. Within the isotropic continuum elastic model and shallow island approximation, energy minimization leads to the following expression of hut formation energy [3]:

$$E = 4\Gamma V^{2/3} \tan^{1/3}\theta - 6cV \tan\theta, \qquad (1)$$

where Γ represents the increase of surface energy. In the presence of a wetting layer, $\Gamma = \gamma_h \csc\theta - \gamma_w \cot\theta$ [3], where γ_h and γ_w are, respectively, energy per area of the hut and wetting-layer surface. $V \approx h^3 \cot^2\theta$ is the hut volume. $c = (M_{\mathrm{Ge}}\varepsilon)^2(1-\nu)/2\pi G_{\mathrm{Si}}$, where M_{Ge} and ε are, respectively, Young's modulus and the misfit strain of the Ge film, and ν and G_{Si} are, respectively, the Poisson ratio and shear modulus of the Si substrate.

There are two possible mechanistic pathways leading to hut formation: one through a thermally activated nucleation process [3,8] and the other through a barrierless process [10–13] in which *faceted* huts transform naturally from *nonfaceted* "prepyramids" in the form of mounds or stepped islands. If huts form via the nucleation, there exists a critical size of nucleus, beyond which huts favor growth over decay. If huts form via the transformation, there exists a minimum size (may not be "critically"

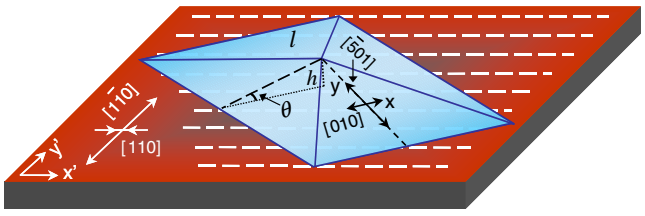

FIG. 3 (color online). Schematics of a square-based Ge hut on Si(001). Arrowed crosses indicate surface stresses.

defined), beyond which huts become more stable than prepyramids. Below, we estimate the critical size for hut nucleation.

For a pure Ge hut, the constant c can be calculated from the misfit strain ($\varepsilon = 0.042$) and elastic constants of Si and Ge, and we obtain $c = 0.27$ meV/Å^3. To calculate Γ, we use the results in Fig. 1. Because huts are sufficiently large with at least 3 layers of Ge [normalized to (001) orientation], we use the converged Ge/Si(105) surface energy as the hut surface energy, $\gamma_h = 61.4$ meV/Å^2 [20]. For a Ge wetting layer, we use $\gamma_w = 61.3$ and 60.7 meV/Å^2, corresponding, respectively, to the energies of Ge/Si(001) with 4 and 5 layers of Ge. This choice is made by considering the (105)-faceted hut forms to replace the fourth and fifth layers of Ge on Si(001) as the wetting-layer thickness is 3 [1,18]. We note that the surface energy of Ge/Si(001) decreases continuously with increasing Ge coverage with values of 71.3, 64.4, 62.5, 61.3, and 60.7 meV/Å^2 at 1, 2, 3, 4, and 5 layers of Ge, respectively. It varies with Ge layer thickness due to surface and interface interaction. Thus, it is inappropriate to use the converged Ge/Si(001) or the pure Ge(001) surface energy as the wetting-layer surface energy [20].

Using the above values of γ_h, γ_w, and c, we estimate, for a pure Ge hut, $h_c \approx 4\Gamma/9c \sim 11$–$16$ Å, or $l_c \sim 110$–160 Å. This agrees very well with the minimum Ge hut size observed by several different experimental groups [6–10]. In Fig. 4, we plot Eq. (1) (solid curve), illustrating the quantitative dependence of energy on hut volume [3], scaled to the critical volume $V_c \sim 6 \times 10^4$ Å^3 and energy barrier $E_c \sim 9 \times 10^3$ meV.

Furthermore, we may assess the quantitative trend of critical size for SiGe alloy huts. Considering that the top surface layers remain as pure Ge for the alloy hut and wetting layer due to Ge surface segregation [18], the change of surface energy will be mainly caused by reduced compressive strain in the alloy. Because both the Ge(105) and Ge(001) surface energies increase almost linearly with decreasing compressive strain [19], their difference and hence the parameter Γ will exhibit a weak strain dependence. Consequently, the critical size of the SiGe alloy huts depends on strain mainly through constant c as $h_c \sim \varepsilon^{-2}$ [3]. It increases quadratically with decreasing strain, or Ge concentration. For a 25% Ge alloy, we estimate that the critical size becomes $h_c \sim 216$ Å, or $l_c \sim 2160$ Å. Indeed, experiments have shown that the SiGe alloy huts [12–14] are generally much larger than pure Ge huts [6–10].

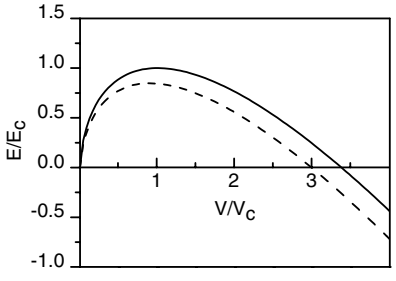

FIG. 4. The hut formation energy as a function of volume. The solid curve is from Eq. (1) without the edge term; the dashed curve is from Eq. (3) with the edge term.

The quantitative information we obtain also sheds new light to the understanding of the mechanisms underlying hut formation. A Ge hut with a height of $h \sim 16$ Å contains $\sim$6800 atoms, while a SiGe hut of $h \sim 216$ Å contains $\sim 2.3 \times 10^7$ atoms. This may suggest the hut is unlikely to form via nucleation mechanism because much too large thermal fluctuation involving too many atoms is required, especially for SiGe alloy huts. Before reaching so many atoms, other nonfaceted prepyramids shall form first as continuum mounds or stepped islands due to thermodynamic or kinetic surface roughening; they are stable or metastable against decay and later transform into huts as observed in experiments [10–14].

We point out that one should focus more on the quantitative trends than the exact values we obtained here. For example, the critical size should be a rather rough estimate considering the numerical uncertainty of the calculations and the approximations made in the analysis. Because the surface energy differences between strained Ge(105) and (001) are close to the computational accuracy of a couple of meV, variations in layer thickness and strain might even lead to "negative" Γ [4]. However, the experimental observation of minimum hut size larger than $V_c \sim 6 \times 10^4$ Å^3 suggests a negative Γ is unlikely, because it would imply barrierless nucleation of much smaller huts.

Other important aspects neglected in our analysis include composition and strain variation in the hut and wetting layer. For example, alloying in the hut may increase Ge(105) surface energy, and hence making Γ more positive. Also, the compressive strain at the top apex of the hut is partially relaxed, increasing the local surface energy and stress of Ge(105), while it is enhanced at the edge, decreasing the local surface energy and stress of both Ge(105) and Ge(001).

Finally, we use the calculated first-principles surface stress tensors to address the significance of island edge effect. There can be two edge energy terms: one is the local edge formation energy (analogy of step energy) and the other is the elastic edge relaxation energy due to surface stress discontinuity [4]. The first term might be neglected for a large hut. The second term, which we evaluate here, can be significant. Especially, it may induce a stable island size against coarsening [4].

At island edge, the Ge hut and the wetting layer have about the same thickness on Si(001), i.e., 3 layers of Ge. Hence, we use the calculated stress tensors corresponding to this thickness [20] from Fig. 2. In Ge/Si(105), the stresses along the principal axes are $\sigma^h_{xx} = \sigma^h_{\langle 105\rangle} = 83.4$ meV/Å^2 and $\sigma^h_{yy} = \sigma^h_{\langle 100\rangle} = 42.0$ meV/Å^2; in Ge/Si(001), they are $\sigma^w_{x'x'} = \sigma^w_{\langle 1\bar{1}0\rangle} = 79.1$ meV/Å^2 and

$\sigma^w_{y'y'} = \sigma^w_{\langle 110\rangle} = -5.3$ meV/Å^2. Note that the principal axes in the two surfaces are rotated with respect to each other by $\phi = 45°$. Consequently, to calculate the stress discontinuity at the hut edge, we must first rotate the coordinate system of the wetting layer, transforming its stresses into the $\langle 105\rangle$ and $\langle 100\rangle$ directions as follows:

$$\begin{pmatrix} \sigma^w_{xx} \\ \sigma^w_{yy} \end{pmatrix} = \begin{pmatrix} \cos^2\phi & \sin^2\phi \\ \sin^2\phi & \cos^2\phi \end{pmatrix} \begin{pmatrix} \sigma^w_{x'x'} \\ \sigma^w_{y'y'} \end{pmatrix} = \begin{pmatrix} 0.5 & 0.5 \\ 0.5 & 0.5 \end{pmatrix} \begin{pmatrix} 79.1 \\ -5.3 \end{pmatrix} = \begin{pmatrix} 36.9 \\ 36.9 \end{pmatrix}. \quad (2)$$

(For simplicity, we neglect the shear stress components of the wetting layer after transformation.) It is interesting to see that, although the wetting-layer stress tensor is highly anisotropic [17] in the original coordinate system, it coincidentally becomes isotropic after transformation. As a result, the stress discontinuity is the same around all four edges of the hut, greatly simplifying the analysis.

So, the stress discontinuity in the direction perpendicular to island edge is $F_\perp = \sigma^h_{xx} \cdot \cos\theta - \sigma^w_{xx} = 44.9$ meV/Å^2 and $F_\parallel = \sigma^h_{yy} - \sigma^w_{yy} = 5.1$ meV/Å^2 (negligible). Using $F_\perp$, we add the elastic edge relaxation energy [4] to Eq. (1):

$$E = 4\Gamma V^{2/3}\tan^{1/3}\theta - 6cV\tan\theta - 8C'V^{1/3}\cot^{1/3}\theta \ln(2V^{1/3}\cot^{1/3}\theta/a), \quad (3)$$

where $c' = F_\perp^2(1-\nu)/2\pi G_{\mathrm{Si}}$ and $a = 3.84$ Å are set equal to surface lattice constant. In Fig. 4, we plot Eq. (3) (dashed curve), illustrating quantitatively the effect of this edge energy term for a pure Ge hut. It shifts the critical size to a smaller value. However, it does not induce any stable island size. Therefore, for Ge huts, the elastic edge relaxation energy is likely too small to be effective for self-assembly of huts with uniform size.

In conclusion, we present a comprehensive quantitative analysis of formation and stability of Ge hut formation on Si(001). We show that compressive strain makes the surface energy of Ge/Si(105) to be degenerate with that of Ge/Si(001), leading to (105) faceting on the hut. By combining first-principles calculation with continuum modeling, we are able to estimate the critical size for hut nucleation or formation, which agrees very well with experiments, and to provide a quantitative assessment on the elastic edge relaxation energy due to stress discontinuity, which shows to be too small to induce a stable Ge hut size. Our study has brought new quantitative insights to the understanding of Ge hut formation and stability. With the increasing computing power, we expect such quantitative analysis will be generally applicable to other systems as well.

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[20] The hut island actually forms on Si(001), but for simplicity, we used the surface energy of Ge(105) strained on Si(105) because it is impractical at present to directly calculate the (105)-faceted Ge hut on Si(001). This should be a good approximation as only a small error is introduced in the Ge/Si interface energy. We also note that, because surface energies and stresses depend on Ge layer thickness on Ge/Si(105) and (001) surfaces, it is inappropriate to use the pure Ge(105) and (001) surface energies, while their surface stresses are not even defined without fixed thickness.