

Stability of strained H:Si(105) and H:Ge(105) surfaces

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We report atomic scale studies of the effect of applied strain and hydrogen environment on the reconstructions of the (105) Si and Ge surfaces. Surface energy calculations for monohydride-terminated (001) and (105) reconstructions reveal that the recently established single-height rebonded model is unstable not only with respect to (001) but also in comparison with other monohydride (105) structures. This finding persists for both Si and Ge, for applied biaxial strains from -4% to 4% , and for nearly the entire relevant domain of the chemical potential of hydrogen, thus providing thermodynamic arguments for the experimentally observed H-induced destabilization of the Ge/Si(105) surface. © 2006 American Institute of Physics.

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The epitaxial system Ge/Si(001) has been the focus of intense investigations for more than two decades, acting both as a test bed for our fundamental knowledge of the strained-layer growth mode, as well as a technological launching pad for promising optoelectronic devices based on Ge/Si quantum dots. While the understanding of quantum dot formation has advanced rapidly,¹ the desire to further diversify and control the growth morphologies has triggered studies of Ge/Si epitaxy in the presence of other species. In particular, hydrogen has been shown to have a surfactant effect on the deposition of Ge on low-index silicon surfaces: the island formation is suppressed in the presence of atomic hydrogen, with the growth switching to a layer-by-layer mode.^{2,3} In the H-mediated Ge/Si(001) epitaxy, Si atoms tend to segregate at the surface, and their exchange with Ge atoms is reversible upon hydrogen desorption.⁴ Recently, experiments have broken new ground to address the influence of hydrogen on high-index epitaxial systems. Fujikawa *et al.* used scanning tunneling microscopy and electron energy loss spectroscopy to investigate the H adsorption on Ge/Si(105), and demonstrated the destabilizing effect of hydrogen on the surface.⁵

Motivated by these compelling experiments,⁵ we have studied the influence of applied biaxial strain and chemical potential of hydrogen on the energy of (105) and (001) reconstructions. Our calculations for Si and for Ge surfaces predict that for a wide range of applied strain and chemical potential of H atoms, the single-height rebonded structure⁶⁻⁹ with monohydride termination has higher surface energy than the H-terminated (001). Interestingly, this rebonded-step structure [RS (Ref. 7) or SR (Ref. 9)] also becomes unstable with respect to the single-height unrebonded (SU) model that was originally proposed for the configuration of (105) hut facets.¹⁰ Apart from SU and SR, we have studied all other (105) structures reported so far;^{11,12} for brevity, we present here the results for only two additional models, DT and DU. While both models have double-height steps, they have different atomic bonding at the surface: DT is rebonded and occurs as a *transitional* state in the annealing of SU towards the SR structure,¹² while DU is unrebonded with a large density of dangling bonds at the surface.¹¹ The (mono)hydro-

generated SR, SU, DT, and DU reconstructions are depicted in Fig. 1.

Using the Tersoff potential¹³ parametrized for the Si-H and Ge-H systems,^{14,15} we have performed full relaxations of 150-Å-thick periodic slabs with either clean or H-passivated reconstructions under applied biaxial strains ϵ in the range of $-4\% \leq \epsilon \leq 4\%$. With the dependencies on strain (ϵ) and H chemical potential (μ_H) made explicit, the surface energy γ of a hydrogenated reconstruction has been calculated as

$$\gamma(\epsilon, \mu_H) = [E(\epsilon) - N\mu(\epsilon) - N_H\mu_H]/A(\epsilon), \quad (1)$$

where E is the total energy of the slab of area A , N is the number of Si or Ge atoms, N_H is the number of H atoms passivating the surface, and μ is the chemical potential (bulk cohesion energy) of the Si or Ge atoms. Guided by experiments,⁵ we have only considered here monohydride terminations and estimated the range μ_H for which this type of surface passivation becomes thermodynamically preferred. The lowest value μ_H at which a H-terminated surface becomes favorable over the pristine one is only weakly dependent on the reconstruction and strain, so we use one chemical potential range for each material: $-3.1 \text{ eV} \leq \mu_H \leq 0.0 \text{ eV}$ for Si and $-2.8 \text{ eV} \leq \mu_H \leq 0.0 \text{ eV}$ for Ge.¹⁶

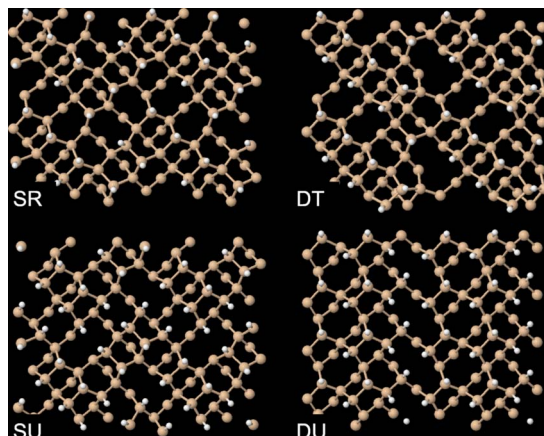


FIG. 1. (Color online) Monohydride (105) reconstructions with two different densities of hydrogenated bonds (Hb), $1.57 Hb/a^2$ (SR, DT) and $2.35 Hb/a^2$ (SU, DU), where a is the bulk lattice constant of Si or Ge. The hydrogen atoms are shown as smaller white spheres.

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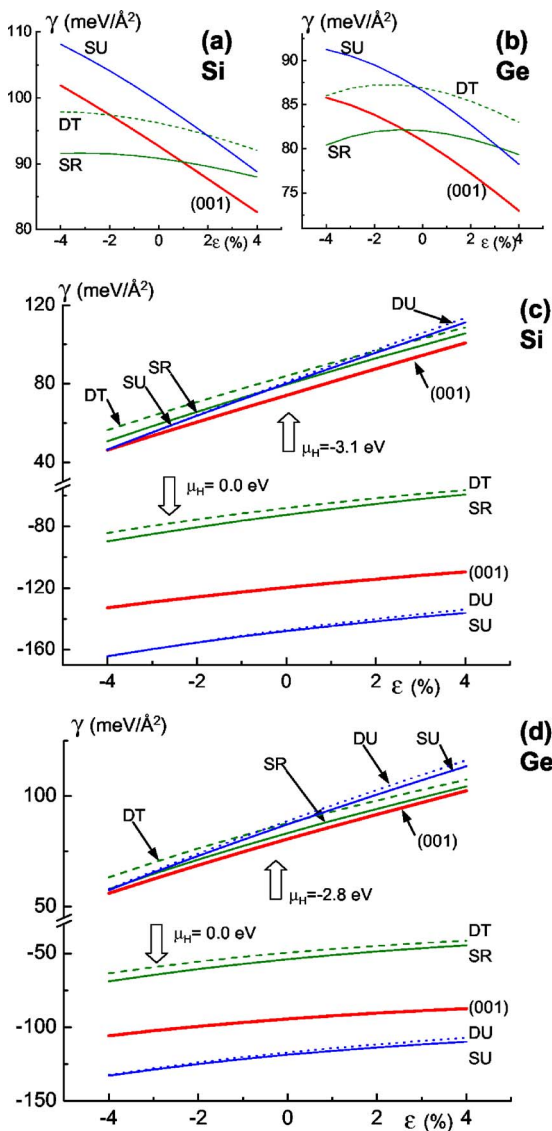


FIG. 2. (Color online) Surface energies (in $\text{meV}/\text{\AA}^2$) of clean [(a) and (b)] and monohydride [(c) and (d)] Si and Ge surfaces plotted vs biaxial strain ϵ (in %). (c) and (d) show surface energy curves for two values of the H chemical potential. The energies of double-step structures are plotted as dashed (DT) or dotted lines (DU). The crossing between SR and (001) curves [present in (a) and (b)] largely disappears when the surfaces are monohydride passivated [(c) and (d)].

Our main findings are summarized in Fig. 2, which shows the energies of Si and Ge surfaces as functions of the biaxial strain ϵ . The results for clean surfaces [Figs. 2(a) and 2(b)] are consistent with previous studies^{9,11,17} which emphasized that the SR reconstruction stabilizes under compressive strain. Referring to Figs. 2(c) and 2(d), in the case of hydrogenated Si and Ge surfaces we have found that (a) upon hydrogenation, the surface energy of SR-(105) becomes lower than that of (001)- 2×1 for both Si and Ge and for nearly the entire ranges of ϵ and μ_{H} defined above; (b) different (105) reconstructions have surface energies whose plots versus ϵ are grouped (bunched) according to the number of hydrogenated bonds per area (e.g., SR and DT, and SU and DU); and (c) the slope $\partial\gamma/\partial\epsilon$ is positive for all monohydride reconstructions, irrespective of what its sign was for clean surfaces.

On general grounds, observation (a) appears consistent with *ab initio* calculations⁵ which estimate that the average

TABLE I. Surface energy ratios for monohydride reconstructions at $\epsilon=0.0$ and $\mu_{\text{H}}=0.0$ eV, compared to the ratios of densities ρ of H-passivated bonds.

	SU/(001)	(001)/SR	SU/SR	SR/DT
γ ratio, Si	1.24	1.65	2.04	1.07
γ ratio, Ge	1.26	1.75	2.20	1.09
ρ ratio	1.18	1.27	1.50	1.00

binding energy of H on Ge/Si(105) is 0.1 eV smaller than that of H on Ge(001). However, such estimate may not readily translate into a difference (or into a ratio) between the surface energies of H-terminated SR and (001). We therefore further pursue the origins of the reversal of the energetic ordering of SR and (001) upon hydrogenation. The *ab initio* binding energy of the Ge-H bond¹⁵ is 2.83 eV, only slightly smaller than that of the Si-H bond. Since this binding energy is an order of magnitude larger than the difference in average binding of H on Ge/Si(105) and H on Ge(001), the key factor in determining the energetic ordering of monohydride reconstructions is the *number of passivated bonds per area*. Indeed, if we focus on surface energies at $\epsilon=0\%$ and $\mu_{\text{H}}=0.0$ eV, we find that their relative ratios can be largely accounted for by the ratios of the corresponding densities $\rho=N_{\text{H}}/A$ of monohydride bonds, as shown in Table I for both Si and Ge. Thus, the SR structure becomes (thermodynamically) unstable with respect to (001) mainly because it has a lower density of H bonds (Hb) at the surface (i.e., $1.57 Hb/a^2$ as compared to $2.00 Hb/a^2$ for the (001)- 2×1 , where a is the bulk lattice constant of either Si or Ge).

Continuing the discussion at $\mu_{\text{H}}=0.0$ eV, when the H-bond density ρ is the same for two different reconstructions, then their energetic ordering is determined by subtler differences in surface stress and in adsorption (binding) energy of H. In general, these factors have less influence on the surface energies than the H-bond density (refer to Table I), which is why, e.g., the SR and DT curves are bunched together and are relatively far from the other surface energy curves at $\mu_{\text{H}}=0.0$ eV (Fig. 2). We have found that this bunching trend [i.e., observation (b) above] holds for all the (105) reconstructions¹² that have the same density of passivated bonds.

Variations of μ_{H} in the stated ranges lead, via Eq. (1), to variations of the energetic separation between same ρ bunches, but leave the surface energy gaps within each bunch unchanged (e.g., the gap between SR and DT does not depend on μ_{H}). Because the lower bounds of μ_{H} necessarily have absolute values that are similar to the Si-H or Ge-H binding energies, the surface energy gap between equal ρ bunches can be wiped out in those limits [refer to the curves corresponding to $\mu_{\text{H}}=-3.1$ eV and $\mu_{\text{H}}=-2.8$ eV in Figs. 2(c) and 2(d)]. On the other hand, an increase of μ_{H} by ~ 0.5 eV above the lower bounds of μ_{H} is sufficient for the bunches to be clearly distinguishable, thus for the density of passivated bonds to set in as the dominant factor for surface energetics.

We now turn to discussing observation (c) listed above. The positive slope of the surface energies in Figs. 2(c) and 2(d) is directly related to an increase in the diagonal components of the surface stress of upon hydrogenation. We have calculated the surface stress components σ_{ij} ($i=1,2;j=1,2$) for all clean and monohydride Si (001) and Si(105)

models and found that each of the two diagonal components σ_{11} and σ_{22} increases by as much as 40.0–65.0 meV/Å² upon hydrogenation. In the case of Ge surfaces, the trend is the same but the increases are smaller, in the range of 15.0–25.0 meV/Å². Noting that stress components do not depend on μ_{H} , the increase of σ_{11} and σ_{22} is caused by the stretching of surface bonds. Indeed, we have verified for Si surfaces that the length of the dimer bonds is stretched by about 2.5% upon passivation, while the bridge bonds made by the rebonded atoms increase by about 1.6%. On Ge surfaces, dimers are stretched by 2.0% and bridges by 0.8% after H adsorption, which explains the smaller increase in the stress components for germanium. *Ab initio* calculations on H:Ge/Si(105) indicate that the bridge bonds actually decrease by 1.5% for the Ge/Si(105) system,⁵ which is also consistent with the smaller stress variations for the Ge surfaces compared to the Si ones.

Before concluding, we comment as to why the empirical potentials are able to capture the main energetic trends for monohydrogenated (105) and (001) surfaces. We note that Tersoff¹³ potentials have already been found to predict the correct lowest-energy (105) reconstruction and strain behavior in the absence of hydrogen,^{8,9,11,17} although most surface energy gaps were overestimated. For passivated surfaces, the hybridization state of all atoms is *sp*³ (as shown in Ref. 5), so major departures from the fitting databases of these potentials do not occur. Subtle electronic effects are therefore unlikely to dominate the surface energy ordering of various monohydride reconstructions, thus rendering the problem of their relative stability tractable at the level of Tersoff potentials.^{13–15} We hope that the results reported here will be followed by further studies at the *ab initio* level, and we expect quantitative improvements to emerge mainly for comparisons between clean and H-passivated surfaces.

In conclusion, we have investigated the relative stability of strained (105) reconstructions with monohydride terminations. On purely thermodynamic grounds, our calculations would suggest that the monohydride H:Ge/Si(105)-SR structure is unstable for any Ge or Si–Ge coverage (or applied strain), not only for coverages below a threshold value. However, the close control of the hydrogen coverage and the energy barriers against SR decaying into other H-passivated reconstructions make the H:Ge/Si(105) experimentally observable as described in Ref. 5. Since the SU model has the largest possible surface density of monohydrides and a structure based on single-height steps, it has been found here to also have the lowest surface energy for the relevant ranges of strain and H chemical potential. It is conceivable that the SU model might be observed experimentally by pursuing different surface preparation recipes that diminish the influence of

kinetics while avoiding the formation of dihydrides. The results presented here could therefore be relevant for future experiments on the Si(105) surface, which has long been known to be rough and disordered at the atomic scale.^{7,18} If maximal monohydride coverage can be achieved on Si(105), the present results suggest that Si(105) could become ordered in the presence of H, with a reconstruction given by the SU model.

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