The 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 to 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 an explanation for the recently observed H-induced destabilization of the Ge(105) surface.

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 understanding of the strained-layer growth, as well as a technological launching pad for promising optoelectronic devices based on Ge/Si quantum-dots. While the understanding of the formation of quantum dots (islands) has progressed rapidly [1], the desire to further diversify and control growth morphologies has triggered studies of Ge/Si epitaxy in the presence of other species. In particular, hydrogen was shown to have a surfactant effect on the deposition of Ge on low-index silicon surfaces: the island formation was suppressed in the presence of atomic hydrogen, with the growth switching to the 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 ground in a different direction to address the influence of hydrogen on high-index epitaxial systems. Fujikawa and coworkers 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 surface energy of (105) and (001) reconstructions of Si and Ge. Our model potential calculations predict that for a wide range of applied strain and H chemical potential, the single-height rebonded [6, 7, 8, 9] structure with monohydride termination has higher surface energy than the H-terminated (001). Interestingly, this rebonded-step structure (RS [10] or SR [6]) also becomes unstable with respect to the single-height unbonded (SU) model that was originally proposed for the configuration of (105) hut facets [11].

In addition to SU and SR, we have studied all other (105) structures [11, 12] although, for brevity, we report results only for the SU, SR, DT, and DU models (depicted in Fig. 1). Using the Tersoff potential [13] parameterized 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 $\epsilon$ in the range $-4% \leq \epsilon \leq 4%$. With the dependencies on strain ($\epsilon$) and H chemical potential ($\mu_H$) made explicit, the surface energy $\gamma$ of a hydrogenated reconstruction has been calculated as

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

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 $\mu$ 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 $\mu_H$ for which the surface hydrogenation becomes thermodynamically favorable. We found that the lowest value $\mu_H$ at which an H-passivated surface becomes favorable over the pristine surface is only weakly dependent on the reconstruction and strain, so we use one chemical potential range for each material: $-3.1$ eV $\leq \mu_H \leq 0.0$ eV for Si and $-2.8$ eV $\leq \mu_H \leq 0.0$ eV for Ge [10].

Our main findings are summarized in Fig. 2 which shows the energies of Si and Ge surfaces as functions of strain and chemical potential.
TABLE I: Surface energy ratios of monohydride reconstructions at $\epsilon = 0$ and $\mu_H = 0.0$ eV, compared to the ratios of densities $\rho$ of passivated bonds.

|                  | (001)/SR | (001)/DT | SU/SR | SU/DT | SR/DT |
|------------------|----------|----------|-------|-------|-------|
| $\gamma$ ratio   | 1.24     | 1.65     | 2.04  | 1.07  |       |
| $\gamma$ ratio   | 1.26     | 1.75     | 2.20  | 1.09  |       |
| $\rho$ ratio     | 1.18     | 1.27     | 1.50  | 1.00  |       |

(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) is consistent with ab initio calculations which estimate that the average binding energy of H on Ge/Si(105) is 0.1 eV smaller than that of H on Ge(001) \cite{5}. Still, this estimate may not translate readily into a surface energy difference (or ratio) between the monohydride terminated SR and (001). We therefore pursue further the origins of the reversal of energetic ordering of SR and (001) upon hydrogenation. The ab-initio binding energy of the Ge-H bond is 2.83 eV \cite{15}, somewhat 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 $\mu_H = 0.0$ eV, we find that their relative ratios can be largely accounted for by the ratios of the areal density $\rho = N_H / A$ of monohydride bonds, as shown in Table I for both Si and Ge. Thus, the SR structure becomes unstable with respect to (001) mainly because it has a lower density of H-bonds \cite{15} at the surface (i.e., $1.57 Hb/a^2$ as opposed to $2.00 Hb/a^2$ for (001), where $a$ is the bulk lattice constant of either Si or Ge).

Continuing the discussion at $\mu_H = 0.0$ eV, when the H-bond density $\rho$ is the same for two different reconstructions, then their energetic ordering is dictated by subtler differences in surface stress and in adsorption (binding) energy of H. In general, these factors have less influence on surface energies than the H-bond density \cite{16}, which is why, e.g., SR and DT curves are bunched together and are relatively far from the other surface energy curves at $\mu_H = 0.0$ eV (Fig. 2). We have found this bunching trend \cite{15} for all the (105) reconstructions \cite{12} that have the same density of passivated bonds.

Variations of $\mu_H$ in the stated ranges lead, via Eq. (1), to variations of the energetic separation between same-$\rho$ bunches, but leave the surface energy gaps within each bunch unchanged (e.g., the gap between SR and DT does not depend on $\mu_H$). Because the lower bounds of $\mu_H$ (Fig. 2) necessarily have magnitudes that are similar to the Si-H or Ge-H binding energies, the separation between equal-$\rho$ bunches can be wiped out in those limits.
[refer, e.g., to the curves corresponding to $\mu_H = -3.1$ eV in Fig. 2(c)]. On the other hand, an increase of $\mu_H$ by 0.3–0.5 eV above the lower bounds of $\mu_H$ 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 the observation (c) listed above. The positive slope of the surface energies in Fig. 2(c,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 for all clean and monohydride Si (001) and (105) models and found that each of the two diagonal components $\sigma_{11}$ and $\sigma_{22}$ increases by as much as 40.0–65.0 meV/Å$^2$ 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/Å$^2$. Noting that stress components do not depend on $\mu_H$, the increase of $\sigma_{11}$ and $\sigma_{22}$ 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 is increased by about 1.6%. On Ge surfaces, dimers are stretched by 2.0% and bridges by 0.8%, which explains the smaller increase of stress components calculated for Ge. Ab initio calculations on H:Ge/Si(105) indicate that the bridge-bonds actually decrease by 1.5% for the Ge/Si(105) system, which is also consistent with the smaller stress variations for Ge surfaces compared to Si ones.

Before concluding, we comment as to why the empirical potentials can capture the main energetic trends for hydrogenated surfaces. We note that Tersoff potentials have already been found to predict the correct lowest-energy reconstruction and strain behavior in the absence of hydrogen [9, 11], although most surface energy gaps were overestimated. For passivated surfaces, the hybridization state of all atoms is $sp^3$, and thus major departures from the fitting databases of these potentials do not occur. Subtle electronic effects are therefore unlikely to dominate the energy ordering of various monohydride reconstructions, which renders them tractable at the level of Tersoff potentials [13, 14, 15]. We hope that the results obtained 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 investigated the relative stability of strained (105) reconstructions with monohydride terminations. On purely thermodynamic grounds, our calculations suggest that the monohydride H:Ge/Si(105)-SR structure is unstable for any Ge or Si-Ge coverage (applied strain), not only for coverages below a threshold value. However, the kinetic barriers against SR decaying into other monohydride reconstructions and the compression in the epitaxial layer make the H:Ge/Si(105) experimentally observable as reported in Ref. [12]. 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. Thus, it is conceivable that the SU model may be confirmed experimentally by pursuing different surface preparation recipes that diminish the influence of kinetics while avoiding the formation of dihydrides. The results presented here could also be relevant for future experiments on the Si(105) surface, which has long been known to be rough and disordered on atomic scales [6]. If maximal monohydride coverage can be achieved on Si(105), the present results indicate that Si(105) would become ordered in the presence of H, with a reconstruction given by the SU model.

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fit the coupling constant $\chi_{H-Ge}$ to the ab-initio binding energy and bondlength of Ge-H reported in Q.S.Li, R.H. Lü, Y. Xie, H.F. Schaefer, J. Comput. Chem. 23, 1642 (2002). We have found the closest agreement with the ab-initio parameters for $\chi_{H-Ge} = 0.76$.

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