On the structure of the Si(103) surface

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Although (103) is a stable nominal orientation for both silicon and germanium, experimental observations revealed that in the case of silicon, this surface remains disordered at the atomic scale even after careful annealing. We report here a set of low-energy reconstruction models corresponding to 1×2, 2×2, and 1×4 periodicities, and propose that the observed disorder stems from the presence of several coexisting reconstructions with different morphologies and nearly equal surface energies. The reconstructions found also suggest that the models previously reported in the literature for the (103) orientation have very high surface energies and are thus unlikely to be experimentally observed. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2804080]

In recent years, the high-index semiconductor surfaces have steadily gained in technological and fundamental importance. From the technological standpoint, these surfaces have clear potential to serve as templates for growing linear arrays of nanostructures because they can have a stepped or grooved morphology with characteristic lengths in the nanoscale regime. Some high-index orientations, however, are nominally flat and are often observed to be the facets of the quantum dots formed during heteroepitaxial growth. It is the case, for example, of the (105) facets that bound the pyramidal islands obtained in the Ge/Si(001) system.[1] To date, a number of high-index Si and Ge surfaces have been discovered to be stable,[2] i.e., they do not facet into other orientations.

Among the stable surfaces of Si and Ge that so far have received very little attention from a theoretical perspective are Si(103) and Ge(103). Despite the fact that they have the same orientation, experiments indicate that Si(103) and Ge(103) have very different atomic structures and morphologies.[3] Ge(103) exhibits two-dimensional atomic ordering with a clear periodic pattern,[4,5] while Si(103) remains rough and disordered on the atomic scale even after careful annealing.[3,6] This remarkable difference between Si(103) and Ge(103) is, in itself, a fundamentally interesting problem. Still, because the Si(103) surface is atomically rough and thus very difficult to tackle, so far there has not been sufficient motivation for performing extensive structure studies on this surface. This situation changes with the discovery[7] of the (103) facetted pyramids that appear during the Si overgrowth of the Ge/Si(001) quantum dots. Motivated by the recent experiments of Wu *et al.*,[7] we have set out to find atomic structure models for Si(103). Based on these models, we suggest that the rough and disordered aspect of Si(103) are due to the coexistence of several reconstructions of similar energies and different bonding topologies. Furthermore, the reconstructions presented here provide evidence that the previously reported[4,5] Ge(103)-1×4 models have too high surface energies to be confirmed in experiments.

The structural models for the Si(103) orientation were determined using a genetic algorithm[8] coupled with the highly optimized empirical potential (HOEP) model of atomic interactions of Lenosky *et al.*[9] We have considered three sizes of the computational cell, 1×2, 2×2, and 1×4, which are shown in Fig. 1. The algorithm selects structures based on their surface energy γ, and starts with a "genetic pool" of $p=30$ initially random atomic configurations of the surface slabs. The genetic pool evolves through crossover operations which combine portions of two arbitrarily chosen pool members (parents) to create another structure (child). The child structure is relaxed and retained in the pool if it is different from all existing structures and if its surface energy is sufficiently low.[8] The optimization is performed for each of the possible numbers of atoms (kept constant) that yield

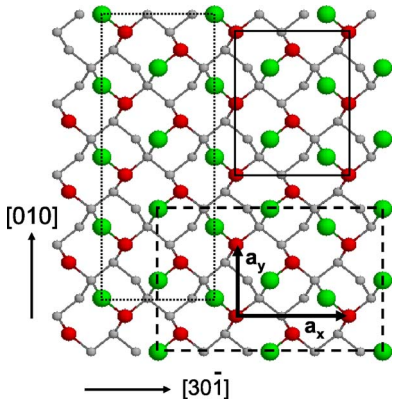

FIG. 1. (Color online) Top view of the bulk truncated Si(103) surface. The larger (green) atoms have two dangling bonds, the intermediate-sized (red) ones have one dangling bond, and the small gray atoms are four coordinated. The unit vectors of the 1×1 unreconstructed primitive cell are $\mathbf{a}_x=a\sqrt{2.5}\mathbf{e}_x$ and $\mathbf{a}_y=a\mathbf{e}_y$, where $a=5.431$ Å is the lattice constant of Si and $\mathbf{e}_x$ and $\mathbf{e}_y$ are the unit vectors along [30$\bar{1}$] and [010], respectively. The rectangles show the unit cells for the 1×2 (solid line), the 2×2 (dash line), and the 1×4 (dotted line) reconstructions.

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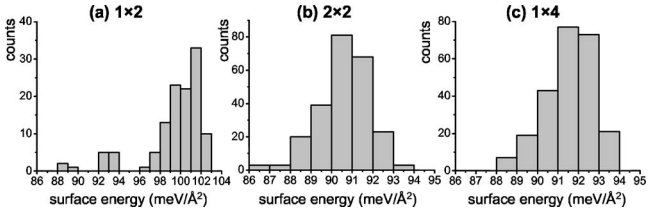

FIG. 2. Histograms of the surface energies retrieved by the genetic algorithm for the (a) Si(103)-1×2, (b) Si(103)-2×2, and (c) Si(103)-1×4 reconstructions.

distinct global minima of a given surface slab. Since there are four atoms in a 1×2 layer (Fig. 1), we have performed four runs for this supercell size and eight runs for each of the other two sizes, 2×2 and 1×4. The surface energies corresponding to the 600 model reconstructions retrieved are organized in the histograms shown in Fig. 2.

To analyze the Si(103) models (Fig. 2), we note that recent studies of high-index Si surfaces suggest that the correct (i.e., experimentally confirmed) structure either has the lowest HOEP surface energy [e.g., Si(105) in Ref. 8] or it has a surface energy that most likely lies within 3–4 meV/Å^2 from the lowest HOEP surface energy value [as in the case of Si(114) and Si(337)].[10,11] Therefore, in order to identify good Si(103) reconstructions, we focus on a surface energy *range* that includes most of the thermodynamically favorable structures, i.e., 86 meV/Å^2 $< \gamma <$ 89 meV/Å^2 (refer to Fig. 2). In this range, there are 35 models across the three periodicities considered (Fig. 1). Of these models, 32 are distinct in the sense that the large period structures (1×4 and 2×2) cannot be reduced to the repetition of a single 1×2 model.

From the 32 distinct structures, we have identified a few pairs of configurations that exhibit minor differences such as bonds relaxing to sightly different local minima but otherwise making up the same topology at the surface. More notably, there are also groups of nearly degenerate reconstructions with markedly different atomic bondings but with nearly equal (and low) surface energies. Some of these reconstructions are depicted in panels (a)–(e) of Fig. 3. We have found that the atomic-scale features that appear frequently on most of the favorable reconstructions (not only those shown in Fig. 3) are the dimers and the rebonded atoms, which would be expected for stepped Si(001) surfaces. Dimers and rebonded atoms occur in a wide variety of relative configurations for any of the low-energy Si(103) reconstructions. Interestingly, the dimer-rebonded atom configuration that is solely responsible for the lowest energy structure of Si(105) (Refs. 12 and 13) is also encountered on Si(103); this configuration is made up of two rebonded atoms that "bridge" at the base of a dimer to form a shape that resembles somewhat the letter ***u***.[14] Figure 3 shows one such ***u*** motif marked in black in panel (b), which can readily be spotted in the other panels as well. Another known motif that appears (though not as frequently as the ***u***) on the low-energy Si(103) reconstructions is the tetramer,[15] denoted by ***t*** in Fig. 3(c).

The similarity between the best Si(103) reconstruction found here [Fig. 3(b)] and the single-height rebonded (SR) model[12] for Si(105) is quite striking, as both models have two ***u*** motifs in their respective unit cells and nearly equal density of dangling bonds, i.e., 1.58 db/a^2 for Si(103) versus 1.57 db/a^2 for SR. Since the unit cells of Si(105)-1×2 and

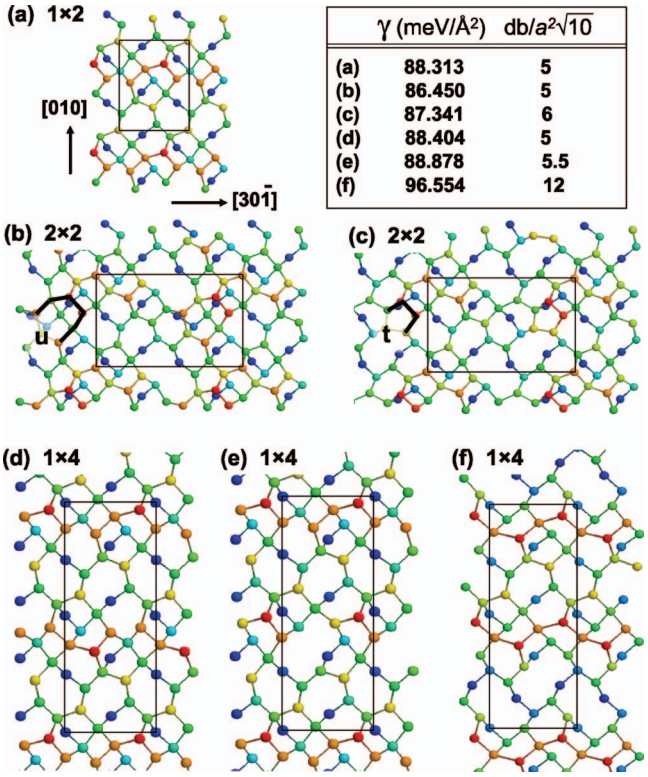

FIG. 3. (Color) Model reconstructions (top views) for the Si(103) surface (a)–(f). Structures (a)–(e) have been obtained in this work, while panel (f) shows the model previously proposed the (103) orientation (Refs. 4 and 5). Atoms are colored according to their coordinates along [103], from red (highest position) to blue (lowest position in the slab shown); the periodic cell is marked by a rectangle in each case. The table (inset) shows the surface energy γ of models (a)–(f) calculated using the Lenosky *et al.* (Ref. 9) potential, and their number of dangling bonds per 1×2 unit area.

Si(103)-2×2 have different sizes, the best Si(103) model allows for an efficient arrangement of its ***u*** motifs at the cost of introducing additional surface stress. Therefore, the resulting lowest surface energy for Si(103) [Fig. 3(b)], 86.45 meV/Å^2, is higher than the surface energy of the SR model,[8] 82.20 meV/Å^2.

The surface stress associated with low-energy Si(103) structures is tensile because most of the bonds are stretched in order to achieve a low dangling bond density. On the other hand, a very large number of dangling bonds per area increases the surface energy even though the atoms at the surface would have significantly more room to relax. This is the case of the reconstruction proposed originally for the Ge(103)-1×4 surface,[4,5] which is shown in Fig. 3(f) after scaling to the lattice constant of Si and relaxation at the HOEP level. The surface energy of the model in Fig. 3(f) is 96.55 meV/Å^2, clearly larger than the surface energy of *any* of the 240 structures accounted for in Fig. 2(c). Even though the main focus of this paper is not on Ge(103), we were intrigued by finding such a high surface energy for model (f) so we recalculated the surface energies of all 1×4 models using an empirical potential for Ge.[16] We have found a surface energy of 91.67 meV/Å^2 for model (f) with the Tersoff potential,[16] while the surface energies of all other 1×4 structures (scaled to the lattice constant of Ge) ranged between 85.94 and 95.02 meV/Å^2. This finding suggests that a re-evaluation of the accepted Ge(103)-1×4 model[4,5] may be warranted in the near future.

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We conclude with a short discussion of the physical implications of having a large number of low-energy reconstructions available for the Si(103) surface. The existence of multiple models with similar surface energies but with very different topologies and different spatial periodicities suggests that it is possible for such models to *coexist* on the Si(103) orientation, a proposal which has recently been made for the case of Si(105) as well.[17] Indeed, experiments to date[6] show that both Si(103) and Si(105) are atomically rough and exhibit no discernable two-dimensional periodicity even after careful annealing. The proposal that several structural patterns can coexist on the same nominal orientation would have little value if any two models placed next to one another on the (103) surface were to give rise to domain boundaries with very high formation energies. However, we have found that *different* 1×2 models do indeed appear next to one another without substantially increasing the surface energy of the reconstructions with larger unit cells; refer, for example, to Fig. 3(e), in which the 1×2 model (a) occupies the upper half of the 1×4 cell while the lower half has a different structure. Since there exists a vast array of energetically favorable motifs made of dimers and rebonded atoms, entropy considerations also support the idea of various structural patterns coexisting on the Si(103) surface.

In summary, we have used a genetic algorithm to find Si(103) reconstructions and proposed that the atomic scale roughness experimentally observed for this surface is due to the coexistence of several nearly degenerate structural models with different bonding topologies and surface periodicities but with similar surface energies. We have found that the low-energy (103) reconstructions largely display the same atomic-scale motifs (combinations of dimers and rebonded atoms) as Si(105),[17] which has lead us to believe that the physical origin of the observed[6] disorder is the same for both Si(103) and Si(105). In the case of Si(105), the structural degeneracy is lifted upon applying compressive strain[17] or through the heteroepitaxial deposition of Ge.[12] For Si(103), it was shown that low coverages of indium can result in the emergence of a preferred reconstruction pattern.[18] The possibility to remove the degeneracy and create a periodic pattern on Si(103) by epitaxially depositing Ge at *low coverage* has not been investigated.[19] If such experiments were to be performed, the calculations presented here predict that the most likely model to emerge is that in Fig. 3(b), which is similar to the SR reconstruction of Ge/Si(105).[12] Upon comparing the structures retrieved by the genetic algorithm with the existing model[4,5] for the Ge(103) surface, we have found that the latter has a density of dangling bonds that is 2.4 times larger than that of the best (103) models. The models presented here[20] can, we hope, play an important role in revisiting the currently accepted structure of Ge(103), as well as in explaining the (103)-facetted islands[7] that appear upon Si capping of the Ge/Si(001) quantum dots.

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