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Ge-dimer relaxation on Si(100)

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We employ *ab initio* total-energy-minimization techniques to study the relaxation of Ge dimers on Si(100). We find that the dimers adopt an asymmetric configuration, in agreement with recent experimental results [E. Fontes *et al.*, Phys. Rev. Lett. **70**, 2790 (1993)]. The average dimer height displacement and tilting angle are found to be 0.79 Å and +19°, respectively. Our calculations predict that the (2×2) and $c(4 \times 4)$ reconstructed structures have the same energy, and suggest that either one of these two could be the ground-state structure.

Because of its relevance to device technology, the Ge-on-Si(100) heteroepitaxial system is of much current interest. Knowledge of the dimer configuration, in particular, is an important first step towards understanding epitaxial growth. Unlike the Si(100) and Ge(100) surfaces, however, which have been the object of several studies,[1–5] only very few experimental measurements have been reported directly addressing the problem of the structure of Ge dimers on the Si(100) surface.[6,7] Low-energy electron-diffraction (LEED) experiments[7] observe that Ge forms a disordered overlayer on the Si(100) surface, but provide no information about Ge dimerization. X-ray–standing-wave (XSW) measurements,[6] on the other hand, find the Ge overlayer to dimerize, with the dimers tilted by an amount of approximately 12.1° with respect to the surface of the substrate. It is therefore of interest to determine the reconstruction state of the Ge/Si(100) surface concurrently with the orientations of the dimers, in order to reconcile the two experimental observations.

We address this problem in the present paper using state-of-the-art *ab initio* total-energy minimization techniques,[8] which have already demonstrated their relevance in the study of covalent semiconductor surfaces.[9] Our calculations reveal, as we will see, that the dimers of Ge on the Si(100) surface are asymmetric, in agreement with recent XSW measurements,[6] suggesting that the Ge-substituted dimer surface behaves in a way entirely similar to that of the bare Si(100) or Ge(100) surfaces, inasmuch as the local structure of the dimers is concerned. We find, also, that the ground-state configuration might be either (2×2), i.e., the same as for Si(100) (taking into account the orientation of the dimers),[5,10,11] or $c(4\times4)$, the two phases having the same energy within numerical accuracy.

As in other studies of semiconductor surfaces,[1,3] we perform our calculations within the framework of the local-density approximation (LDA). We model the Ge/Si(100) system by a slab of eight layers, each containing eight atoms. The atoms in the innermost two layers are held fixed in their ideal bulk positions in order to mimic an infinite crystal, while the other atoms are allowed to move during the relaxation process, as will be detailed below. The supercell, therefore, has two surfaces — one on each side of the slab — consisting solely of germanium atoms. We choose the experimental value of 5.43 Å as the lattice constant, following other *ab initio* calculations.[9,12] (The LDA is known to underestimate slightly equilibrium distances — see Ref. 1.) Periodic boundary conditions are applied in all three Cartesian directions; a vacuum region of width 10.0 Å is used along the z direction, i.e., perpendicular to the surface, which, we verified, is large enough that the interactions between the surface and its images are negligible (i.e., the electron density becomes very small sufficiently far from the surfaces). The nonlocal, norm-conserving pseudopotential of Kleinman and Bylander[13] is used for the silicon cores, while for germanium we choose the local pseudopotential of Starkloff and Joannopoulos,[14] which has been shown to be accurate enough for surface reconstruction studies.[3] We use only the Γ point for sampling reciprocal space, which is sufficient in view of the large size of our supercell. The electronic wave functions are expanded in a plane-wave basis set with an energy cutoff of 8 Ry: it was observed by Dabrowski and Scheffler[1] that for the bare Si(100) surface, an energy cutoff larger than 6 Ry favors buckled dimers over symmetric ones, and we therefore expect that tilting of the Ge dimers on Si (100) will be observed — if it exists — with our choice of energy cutoff.

Starting with a perfect, unreconstructed, (1×1) surface, we first relax the electron wave functions to their ground state, while keeping the atomic positions fixed; we then allow the atoms to relax simultaneously with the electrons until the system reaches a convergent state. The resulting configuration is displayed in Fig. 1. In order to improve the image, two periods of the supercell are shown in each of the x and y directions. It is seen that the surface reconstructs into a $c(2 \times 2)$ structure, with all the dimers tilting in the same direction. Table I lists our calculated values of the average dimer bond length, L, dimer height displacement δz $(= |z_1 - z_2|$, where z_1 and z_2 are the vertical positions of the two sites of the dimers), tilting angle θ, and total energy E for the $c(2 \times 2)$ structure of Fig. 1 (as well as for other phases discussed below), together with the values deduced from XSW measurements by Fontes *et al.* on the basis of a simple rigid-dimer model.[6]

Our calculated bond length $L = 2.48$ Å is smaller than the experimental value of 2.60 ±0.04 Å,[6] but very close to the value of 2.46 Å calculated *ab initio* by Needels *et al.* on the bare Ge(100) surface.[3] This discrepancy is due, in part, to our use of the LDA (which systematically understimates distance,[1] as mentioned earlier) while part of it comes, also, from the fact that our calculation is performed at zero temperature: the dimer bond length is expected to increase with temperature. Similar observations, in fact, hold for the dimer height displacement and the tilting angle, for which we have 0.68 Å and 16°, respectively, in comparison to the experiment values of 0.55 Å and 12.1°. Indeed, it has been observed that the dimer height displacement increases with the decreasing temperature,[6,15] from 0.44 Å at 800 K to 0.55 Å at room temperature. Further, assuming, in order to simplify the calculation, that the dimer bond length is temperature independent, as done by Fontes *et al.*,[6] then, consistent with our results, the tilting angle must increase with dimer height displacement, i.e., with decreasing temperature.

The $c(2 \times 2)$ reconstructed structure we observe here has not frequently been seen experimentally on covalent semiconductor surfaces. Nevertheless, Cardillo and Becker[16] have observed that the $c(2 \times 2)$ structure could coexist with the (2×1) on the bare Si(100) surface. In addition, previous calculations on Si(100) (Ref. 10) have found the energy difference per dimer between the $c(2\times2)$ and (2×1) configurations to be very small, namely 0.067 eV. Whether or not the above situation applies to the Ge/Si(100) surface is not currently known, and we investigate this question next.

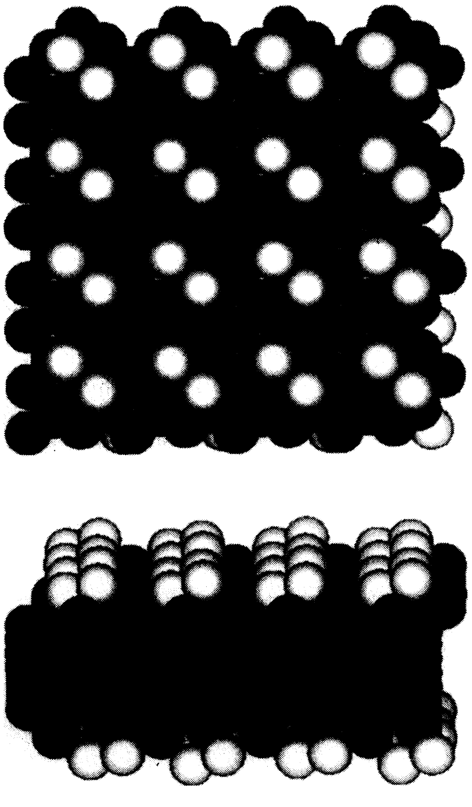

FIG. 1. Top and side views of the $c(2 \times 2)$ reconstructed Ge/Si(100) surface. All eight layers of our sample are shown; germanium atoms are highlighted by using a lighter shade. In order to improve the image, two periods of the supercell are shown in each of the x and y directions.

In order to determine if the $c(2 \times 2)$ structure is the ground state for the Ge/Si(100) system, or simply a metastable state, and see how it compares with the (2×1) structure usually observed on the bare Si(100) surface at room temperature,[16] we have carried out another calculation now using, as the initial configuration, the (2×1) structure, with all the dimers tilting in the same direction. The initial dimer height displacement and tilting angle were set to 0.40 Å and 7.0°, respectively. The fully-converged configuration is shown in Fig. 2. It is clear that the structure has evolved into a $c(4 \times 4)$ configuration, with one dimer out of four tilting in a direction opposite to that of its neighbors. Since we are using the conjugate-gradient technique[8] to relax the system, it is not possible for the system to overcome an energy barrier, however small it is, so that there can be no barrier between the initial (2×1) structure and the final $c(4\times4)$. [We will show below that this $c(4 \times 4)$ structure actually has the same energy, within numerical accuracy, as the (2×1).]

As can be seen in Table I, the average dimer height displacement and tilting angle we find for this new phase, $\delta z = 0.74$ Å and $\theta = 18°$, are very similar to those observed for the $c(2 \times 2)$ structure above, and the same analysis holds upon comparing to experiment. The to-

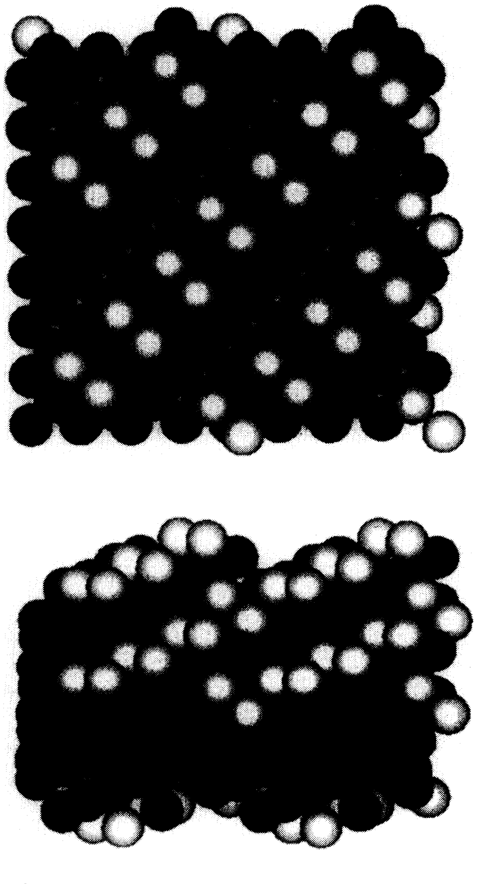

FIG. 2. Same as Fig. 1, but for the $c(4 \times 4)$ configuration.

TABLE I. Average dimer bond length L, dimer height displacement δz, tilting angle θ, and total energy of the system E, for our three reconstructed structures; also shown are the variations in energy per dimer, as measured with respect to the $c(2 \times 2)$ structure, $E_{\rm dimer}$ [$= (E_X - E_{c(2\times2)})/8$ — there are eight dimers in our system, with $X = c(4 \times 4)$ or (2×2)], as well as the corresponding experimental values (where available).

	$c(2 \times 2)$	$c(4 \times 4)$	(2×2)	Expt.[a]
L (Å)	2.48	2.40	2.44	2.60 ± 0.04
δz (Å)	0.68	0.74	0.79	0.55
θ (deg.)	16	18	19	12.1 ± 0.2
E (eV)	-6803.27	-6804.94	-6804.87	...
$E_{\rm dimer}$ (eV)	0	-0.21	-0.20	...

[a] Reference 6.

tal energy of the $c(4 \times 4)$, however, is substantially lower than that of the $c(2 \times 2)$, 1.67 eV, or 0.21 eV per dimer, indicating that the $c(2 \times 2)$ is a metastable state for the Ge/Si(100) surface.

The ground state of the bare Si(100) surface is known to be (2×2) (taking into account the orientations of the dimers with respect to the surface), both from low-temperature scanning-tunneling microscopy measurements[5] and from theoretical calculations.[10,11] In order to determine if this reconstruction phase is also a possible state of the Ge/Si(100) surface, we have performed a third calculation, this time using the (2×2) structure itself as the starting point (and setting $\delta z = 0.58$ Å and $\theta = 10°$). The resulting relaxed configuration is illustrated in Fig. 3: the system is found to be essentially stable in this (2×2) state. In fact, as can be seen in Table I, the parameters characteristic of this configuration are almost identical to those we obtain for the $c(4 \times 4)$, and in particular the energies are virtually equal, within the error bar of the calculation (about 0.02 eV — Ref. 1). This indicates that the surface energy is relatively insensitive to the orientations of the dimers with respect to one another. We can therefore extrapolate that the energy of the (2×1) phase should be similar to that of (2×2) and $c(4 \times 4)$, at least at low temperatures; the (2×1) should occur, therefore, with the same probability as the other two, presumably coexisting on the same surface, though it is not clear under which precise conditions it will exist.

It is interesting to note, from Fig. 3, that the centers of mass of the Ge dimers do not sit on a straight line but, rather, are displaced from their unreconstructed-surface position along the [110] direction, by about 0.21 Å. In addition, we find the dimers to relax inwards (i.e., towards the surface) by about 0.19 Å. The same is true, in fact, of the $c(4 \times 4)$ configuration, Fig. 2. Such displacements have not been detected experimentally, but our observations are consistent with other zero temperature calculations of bare semiconductor surfaces,[3,11,17,18] which predict displacements along [110] in the range 0.17–0.31 Å, and along z in the range 0.03–0.13 Å. This is a definite prediction of our model; the apparent disagreement with experiment again most likely results from our working at zero temperature.

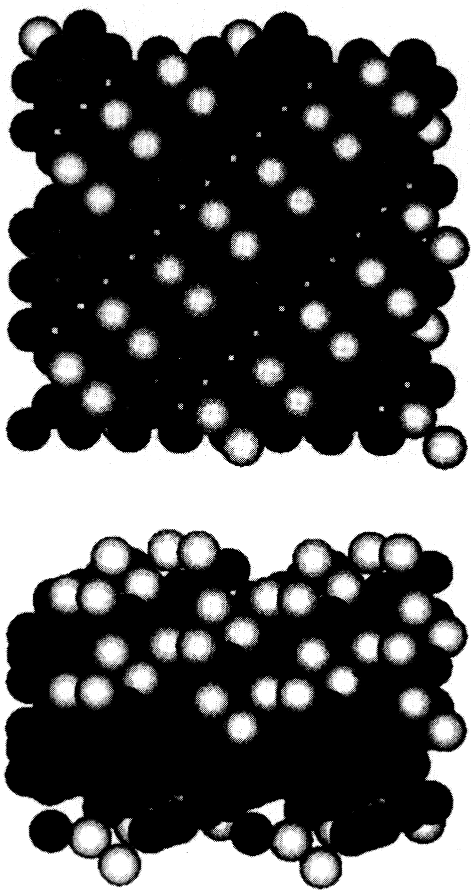

FIG. 3. Same as Fig. 1, but for (2×2) structure.

In summary, by employing state-of-the-art *ab initio* total-energy methods, we have established unequivocally that dimers on the heteroepitaxial Ge/Si(100) surface are tilted, consistent with recent x-ray–standing-wave measurements. We remark that, in all cases examined, the underlying Si substrate remains close to its ideal, bulk-like, configuration. We find, in addition, that the (2×2) and $c(4 \times 4)$ reconstructions have identical energies within the error bar of our calculations, presumably as well as the (2×1), and that any of these three configurations might be the ground state of the system; more detailed calculations are required to resolve this point. The $c(2 \times 2)$ phase, on the other hand, clearly is a metastable state.

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[1] J. Dabrowski and M. Scheffler, Appl. Surf. Sci. **56**, 15 (1992).

[2] R.M. Tromp, R.J. Hamers, and J.E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985); R.J. Hamers, R.M. Tromp, and J.E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[3] M. Needels, M.C. Payne, and J.D. Joannopoulos, Phys. Rev. Lett. **58**, 1765 (1987).

[4] P.C. Weakliem, G.W. Smith, and E.A. Carter, Surf. Sci. Lett. **232**, L219 (1990).

[5] R.A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).

[6] E. Fontes, J.R. Patel, and F. Comin, Phys. Rev. Lett. **70**, 2790 (1993).

[7] H.J. Gossman, L.C. Feldman, and W.M. Gibson, Surf. Sci. **155**, 413 (1985).

[8] M.P. Teter, M.C. Payne, and D.C. Allan, Phys. Rev. B **40**, 12 255 (1989).

[9] I. Stich, M.C. Payne, R.D. King-Smith, J-S. Lin, and L.J. Clarke, Phys. Rev. Lett. **68**, 1351 (1992).

[10] J. Ihm, D.H. Lee, J.D. Joannopoulos, and J.J. Xiong, Phys. Rev. Lett. **51**, 1872 (1983).

[11] N. Roberts and R.J. Needs, Surf. Sci. **236**, 112 (1990).

[12] G. Brocks, P.J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).

[13] L. Kleinman and D.M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

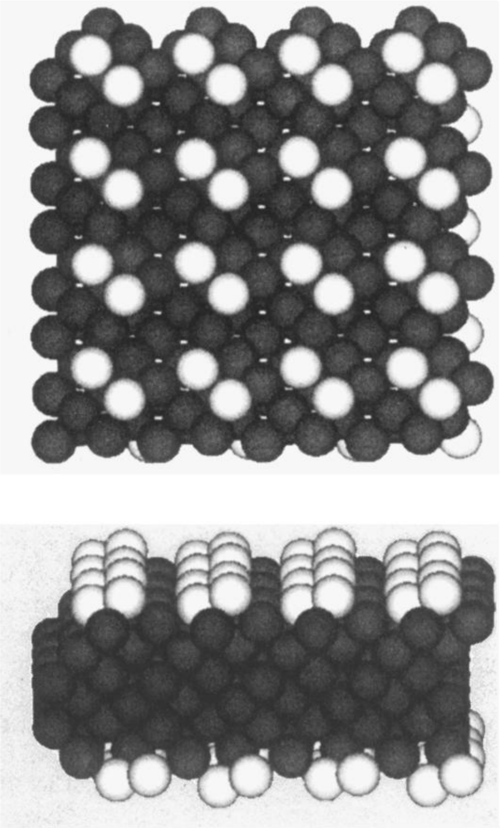
[14] Th. Starkloff and J.D. Joannopoulos, Phys. Rev. B **16**, 5212 (1977).

[15] R. Martinez, E. Fontes, J.A. Golovchenko, and J.R. Patel, Phys. Rev. Lett. **69**, 1061 (1992).

[16] M.J. Cardillo and G.E. Becker, Phys. Rev. B **21**, 1497 (1980).

[17] D.J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[18] M.T. Yin and M.L. Cohen, Phys. Rev. B **24**, 2303 (1981).



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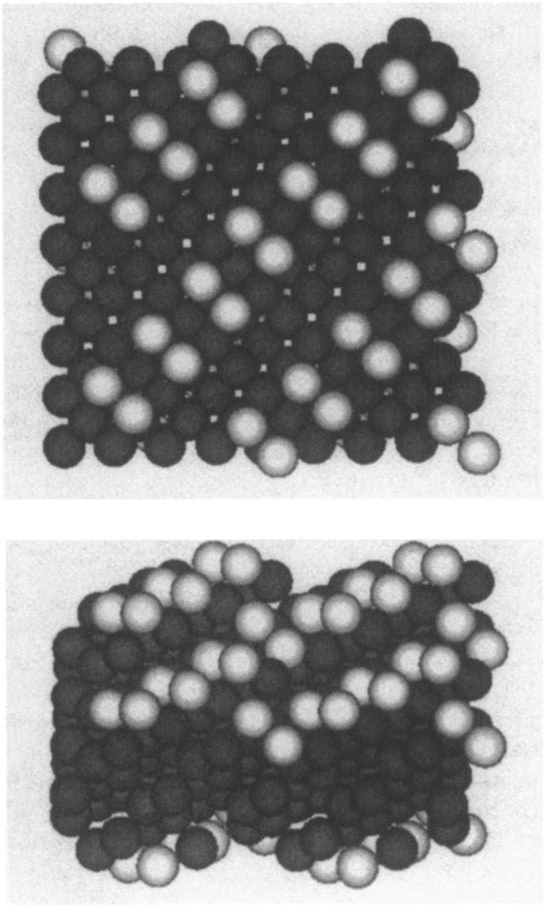
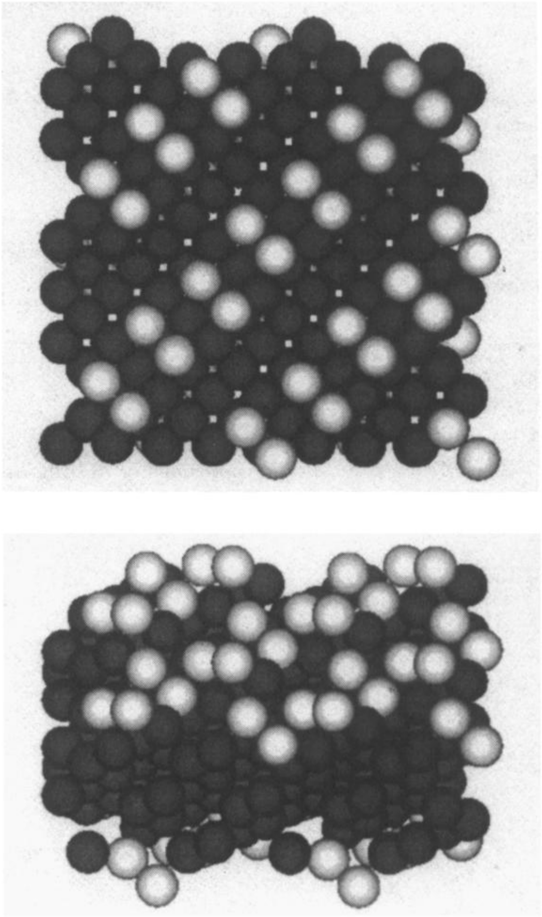


FIG. 2. Same as Fig. 1, but for the $c(4 \times 4)$ configuration.



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