

## Symmetric dimers on the Ge(100)- $2\times 1$ -Sb surface

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We present results of a first-principles total-energy calculations of the  $(2\times 1)$  reconstruction induced by the absorption of a monolayer of Sb on Ge(100). Our calculations show that the Sb overlayer atoms form symmetric dimers, in disagreement with a surface x-ray diffraction (SXD) experiment that found the midpoint of the Sb dimer shifted by  $\sim 0.16$  Å. The calculated structure is similar to the Si(100)- $(2\times 1)$ -Sb surface, with the substrate displacements from bulk positions larger than in Si. The Sb-Sb dimer bond length is in good agreement with SXD and x-ray standing waves experiments. [S0163-1829(97)06704-0]

The adsorption of group-V elements on the surface of the semiconductors Si and Ge has attracted much attention in part because of its interesting applications. It has been found experimentally that these elements can be used as surfactants in the growth of Si-Ge superstructures improving the quality of the interfaces.<sup>1</sup> In addition, the study of this adsorption is important in the understanding of the initial stages of the growth of III-V semiconductors on to Si and Ge.<sup>2</sup> On the (100) surfaces, group-V materials passivate the semiconductor substrate in what appears to be a general rule: the adsorbate atom bonds to two semiconductor dangling bonds and to another adsorbate forming a dimer structure. The remaining two electrons form a lone pair.<sup>3-8</sup> The detailed morphology of the dimers and the reordering of the substrate atoms depend on both the adsorbing group-V material and the semiconductor substrate. The Ge(100) $(2\times 1)$ -Sb surface has been studied using synchrotron photoemission spectroscopy and high-energy electron diffraction,<sup>5</sup> angle-resolved UV photoelectron spectroscopy (ARUPS),<sup>6</sup> surface x-ray diffraction (SXD),<sup>7</sup> and x-ray standing waves (XSW).<sup>8</sup> The experimental evidence is clear: the Ge(100) terminated with 1 ML of Sb reconstructs by the formation of Sb dimers. However, the microscopic atomic structure is not known in detail. There are two structural points of interest for this system that are still unclear. The first concerns the symmetry of the dimers. The SXD study has proposed an asymmetrical dimer to explain its data: the midpoint of the dimer is shifted laterally by  $\sim 0.16$  Å. This asymmetry implies a rehybridization of the Sb electrons. It is, however, not obvious why a rehybridization of this kind should occur. The second point concerns the distance between the Sb and the first Ge layer. In the SXD experiment, the vertical positions of the Sb atoms are almost at the continuation of the Ge bulk plane (0.03 Å below for one atom and 0.01 Å above for the other). The vertical position of the first Ge layer is also similar to the bulk position, making the distance between the Sb plane and the first Ge layer very short (1.39 and 1.43 Å). In the XSW experiment, the first Ge layer is pushed down, while the Sb atoms are 0.14 Å above the continuation of the bulk diffraction planes. The distance between the Sb and the first Ge plane is 2.0 Å, quite different from the SXD value.

Prompted by these conflicting results, we have performed first-principles calculations of the Ge(100) $(2\times 1)$ -Sb surface. The optimum structure is obtained using the Car-

Parrinello molecular-dynamics approach.<sup>9</sup> In this way, the search is not biased by a given model of the surface structure.

Calculations have been performed within the local density approximation to the density functional theory.<sup>10,11</sup> We have used a repeated slab geometry, each slab consisting of 5 layers of Ge atoms, plus a monolayer of Sb atoms. The bottom surface was saturated by hydrogen atoms in a dihydrate structure. Two consecutive slabs were separated by an empty space 9.0 Å wide. The four topmost Ge layers of the slab and the Sb atoms were given full freedom to move, while the fifth layer of Ge and the H atoms were held fixed at the ideal positions in order to simulate a bulklike termination. We have checked the influence of the slab size by increasing the number of Ge layers from five to eight (the first six layers of Ge were allowed to relax). The relaxed atomic coordinates were almost unchanged. Most of our results have been obtained using a  $p(4\times 4)$  supercell with 16 atoms/layer. Only electronic states at  $\Gamma$  have been included, and expanded in plane waves with a kinetic energy cutoff  $E_{\text{cut}}=8$  Ry. We used for Ge and Sb norm-conserving nonlocal pseudopotentials<sup>12</sup> that include *s* and *p* nonlocal terms. They are treated within the Kleinman-Bylander scheme.<sup>13</sup> The Ge pseudopotential has been extensively tested in previous calculations of bulk,<sup>14</sup> liquid,<sup>15</sup> amorphous,<sup>16</sup> and the (111) surfaces of Ge at several temperatures.<sup>17-21</sup> The Sb pseudopotential has been tested in the bulk, and in a previous study of the adsorption of 1 ML of Sb on Ge(111), giving excellent results.<sup>22</sup> Other computational details are as in Ref. 22.

The starting configuration for the simulation was the asymmetric dimer structure of Lohmeier *et al.* Other starting configurations were also tested, arriving at the same final structure. The atomic coordinates were fully relaxed and it was found that the asymmetric dimer structure was not stable. It spontaneously evolved to the symmetric dimer structure shown in Fig. 1(a) with no lateral shift and almost no buckling. Although the calculated dimer is symmetric, its bond length ( $d_D$ )=2.95 Å is in good agreement with the SXD (2.90 Å) value. It is also close to the XSW (3.06 Å) value. In Fig. 1 we show the calculated displacements of the atoms with respect to the ideal bulk positions [Fig. 1(a)], compared with the experimental results of Lohmeier *et al.* [Fig. 1(b)]. As mention before, the main difference between the results of our calculations and the SXD experiments con-

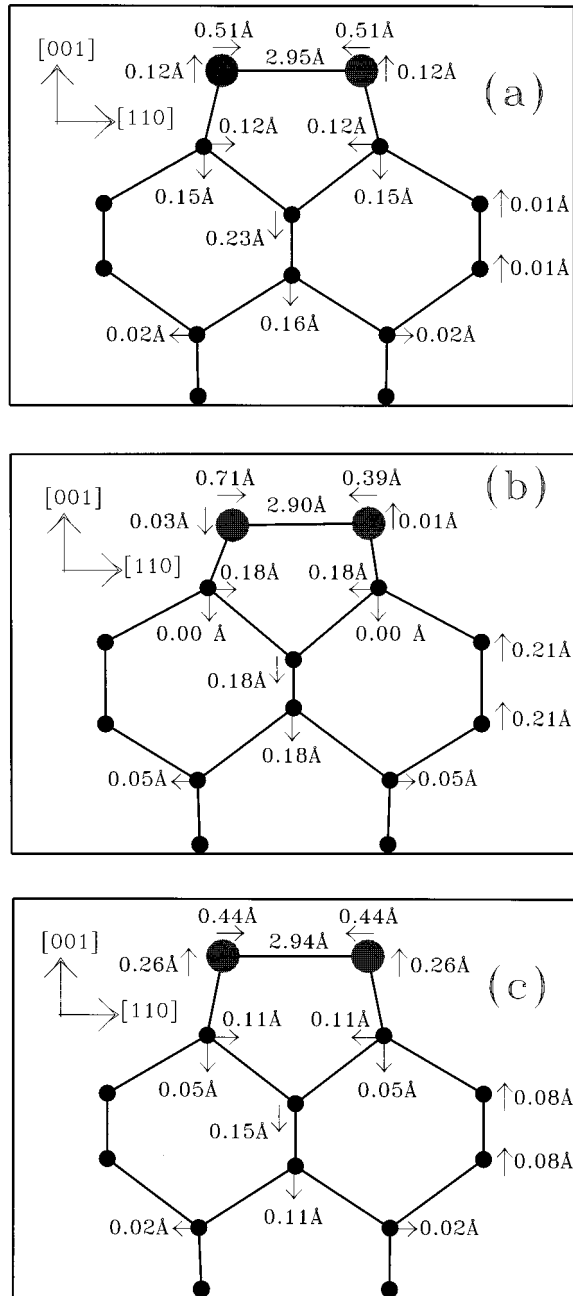


FIG. 1. Side view of the equilibrium atomic structure of (a) Ge(100)-(2 $\times$ 1)-Sb (calculated), (b) Ge(100)-(2 $\times$ 1)-Sb (experimental), (c) Si(100)-(2 $\times$ 1)-Sb (calculated). Small black circles represent Ge atoms, while bigger shaded circles corresponds to Sb atoms.

cerns the symmetry of the Sb dimer. Our calculation shows not only that the ground state of the Ge(111)-Sb-(2 $\times$ 1) is given by a symmetric dimer structure, but also that the asymmetric dimer structure is not stable. There is no reason why the Sb dimer should be asymmetric, although clean Si and Ge(100) show a (2 $\times$ 1) surface reconstruction with the top Si(Ge) atoms forming asymmetric dimers. On these dimers, each atom bonds to the other dimer atom, and with two second-layer atoms, leaving one dangling bond per atom. The total energy can be lowered by a charge transfer from one atom to the other. The more negatively charged atom moves upwards, while the more positively charged atom

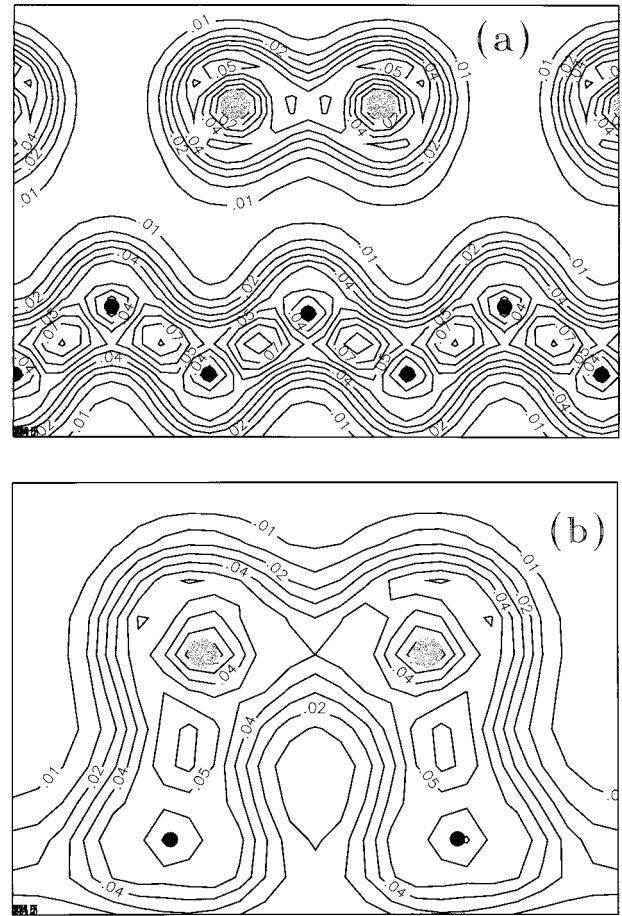


FIG. 2. Total valence charge density of the Ge(100)-(2 $\times$ 1)-Sb surface (a) on the plane cutting vertically through the Sb dimer, and (b) on a plane passing through the Sb dimer and first-layer atoms. Small black circles represent Ge atoms, while bigger shaded circles correspond to Sb atoms.

moves downwards. A similar charge transfer mechanism is not likely to happen in Ge(100)(2 $\times$ 1)-Sb. Each Sb atom has five valence electrons. After binding with two substrate Ge atoms, Sb dimerized with another Sb atom, leaving two electrons that form a lone pair. This atomic configuration is very

TABLE I. Calculated dimer bond length ( $d_D$ ) and back bond length ( $d_{12}$ ) for the Sb/Ge(100)-(2 $\times$ 1) and Sb/Si(100)-(2 $\times$ 1) surfaces in comparison with previous theoretical and experimental results.

|                  | $d_D$ (Å) | $d_{12}$ (Å) |
|------------------|-----------|--------------|
| Sb/Ge(100)       |           |              |
| SXD              | 2.90      | 2.49, 2.47   |
| XSW              | 3.06      | -            |
| This work        | 2.95      | 2.62         |
| Sb/Si(100)       |           |              |
| SEXAFS           | 2.88      | 2.63         |
| Theory (Ref. 23) | 2.93      | 2.61         |
| Theory (Ref. 24) | 2.94      | 2.59         |
| Theory (Ref. 25) | 2.87      | 2.53         |
| This work        | 2.94      | 2.55         |

stable, and our calculations show that the Sb electrons do not rehybridize. So far, to our knowledge, no other experiment has been able to confirm the existence of the shift proposed by the SXD experiment. In the similar system Si(100)(2×1)-Sb the Sb atoms also form symmetric dimers. As observed in Fig. 1(c) the atomic displacements from the bulk ideal structure are very similar to Ge. However, for the case of Si, the atomic positions of the substrate atoms are closer to their bulk positions than in the case of Ge.

Some other differences between our calculations and the SXD experiment can be observed in Fig. 1. According to the SXD coordinates, the Sb and Ge first layers are almost in the ideal bulk terminated vertical position. This makes the experimental bond length between Sb and Ge ( $d_{12}$ ) very short: 2.49 and 2.47 Å (the sum of covalent radii of Sb and Ge is 2.62 Å). In our calculations the Sb atoms are displaced upwards  $\sim 0.12$  Å while first-layer Ge atoms are displaced downwards by  $\sim 0.15$  Å, giving a bond length of 2.62 Å. Our results are in better agreement with the XSW data. Lessmann *et al.* found 0.14 Å for the height of the Sb atoms with respect to the continuation of the bulk (this distance can be measured very accurately with XSW, and it is a unique model-independent result of this method). They also found an inward relaxation of the first-layer atom of  $\sim 0.46$  Å. This value is larger than ours, but it is in the same direction. Also we should keep in mind that in XSW this number depends on the underlying model and the margin of error is large:  $\pm 0.2$  Å.

In Table I we compare our calculated  $d_d$  and  $d_{12}$  for Sb on Ge(100) and Si(100) with several experiments and previous calculations. Besides the  $d_{12}$  of the SXD experiment, the

agreement in bond lengths among theories and experiments is quite good. Also, the differences between Si and Ge are small.

The Sb dimer formation can be clearly observed in the total valence charge density on a plane cutting vertically through the Sb dimer [Fig. 2(a)]. The Ge-Ge bonds are almost bulklike. In Fig. 2(b) we plot the charge density on a plane passing through both the Sb dimers, and the first Ge layer. We can observe that the Sb-Ge bonds are stronger than the Sb-Sb bonds but weaker than the Ge-Ge bonds. With the Sb atoms strongly attached to the Ge surface, and a weaker Sb-Sb bond, a phase transition to a (1×1) surface could happen at higher temperatures. The final phase could be an ordered (1×1) structure, similar to the one reported by Hwang and Golovchenko<sup>26</sup> in Pb on Ge(111), or a disordered structure, with the Sb atoms forming new bonds with other Sb atoms, and losing the (2×1) periodicity. More experimental, and theoretical work about the behaviour of this surface at high temperatures is needed.

In summary, we have performed first-principles total-energy calculations of the Ge(100)(2×1)-Sb surface. The most stable structure shows symmetric Sb dimers, with a bond length of 2.95 Å. Sb atoms are located 0.12 Å above the continuation of the Ge bulk, and the first-layer Ge atoms show an inward relaxation, giving a Sb-Ge bond length of 2.65 Å, similar to the sum of covalent radii.

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