Stability of the $c(4\times8)$ structure in the adsorption of Pb in the (100) surface of elemental semiconductors

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Using first-principles total-energy calculations, we have studied the atomic structure and stability of the $c(4\times8)$ phase of Pb on Ge(100). The structure consists of rows of Pb ad-dimers, with one missing row out of every four, yielding a coverage of 75% of a monolayer. The dimers are asymmetric: there is a relative vertical separation of ~0.81 Å between the two atoms. Surface formation energies show that this configuration is more stable than the full monolayer (2×1) structure. Opposite results are found for Sb on Ge(100), where the (2×1) reconstruction is preferred over the $c(4\times8)$. Our calculations provide some insights into the microscopic origin of the difference in stability between group V and heavy group IV elements adsorbed on the (100) surfaces of the elemental semiconductors Si and Ge. [S0163-1829(98)52136-4]

The adsorption of thin metal overlayers at semiconductor surfaces continues to be the subject of active research not only because of its potential industrial applications, but also because of fundamental physical reasons. In basic research, the interest is motivated by a desire to understand several properties such as surface reconstruction, chemical passivation, Shottky-barrier formations, etc. These phenomena occur not only in metal-semiconductor systems, but also in many other interfaces. Technological applications include, for example, the use of metals as surfactants to improve the quality of epitaxial growth. It is known that a monolayer of Sb or As helps in the growth of thick, low-defect films of Ge on the (100) and (111) surfaces of Si.[1]

When less than one monolayer of group III, IV, or V elements are deposited on the (100) surfaces of Si and Ge, different structures have been observed experimentally. The building block in all these reconstructions is the same, and it consists of metal ad-dimers in the first atomic layer. However, the symmetry of the reconstruction and the detailed atomic structure of the surface depend crucially on the particular metal that is deposited. For example, Sb and As on Si(100) and Ge(100) form (2×1) reconstructions.[2–9] The two atoms of the dimers are symmetric, and the original Si (Ge) dimers are completely broken. On the other hand, when a small fraction of a monolayer of group III elements is grown on Si(100), the adatoms form straight lines of dimers.[10–12] As the coverage is increased, the rows become crowded and the maximum packing density is achieved at half a monolayer. At this point, the metal adatoms form ordered (2×2) phases.[10,11,13] In this configuration, the ad-dimers are also symmetric, and the formation of the new reconstruction occurs without the disruption of the underlying Si-Si dimers. For small amounts of group IV elements (Pb or Sn) deposited on Si(100) and Ge(100), similar behavior has been observed by scanning tunnel microscope (STM) experiments.[14–16] When the coverage is close to half a monolayer, a large variety of structures can be seen. STM images show domains with (2×2), $p(4\times2)$, and $c(2\times4)$ reconstructions. Although the original Si (Ge) dimers are still intact, the ad-dimers are now asymmetric: there is a difference in the vertical positions of the two atoms. With an increase of the coverage, a $c(4\times8)$ (Refs. 14–17) reconstruction is observed. In this structure, the Pb or Sn adatoms form asymmetric dimers. They are buckled in different orientations, and they are arranged in chains along the $(1\bar{1}0)$ direction. Larger deposits of Pb or Sn result in the occupation of a new overlayer. The one monolayer (2×1) structure [the most stable configuration that group V elements form on the (100) surfaces of Si and Ge] is observed only for Pb on Si(100), and, to our knowledge, has never been reported for Pb on Ge(100), or Sn on Si(100) or Ge(100). On the other hand, the $c(4\times8)$ reconstruction is characteristic of the growth of heavy group IV elements on Si(100) and Ge(100), and it has not been observed in the cases of group III or V.

The purpose of this article is to study the atomic and electronic properties of the $c(4\times8)$ structure. Most of our calculations are performed for the case of Pb on Ge(100), and some for Pb on Si(100). Similar results are expected for Sn on Si(100) and Ge(100). From surface formation energies, we find that the $c(4\times8)$ is the stable configuration for Pb on Ge(100), and the (2×1) reconstruction for Sb on Ge(100). These findings are in very good agreement with experimental results.

Calculations have been performed within the Car-Parrinello scheme.[18] A combined electronic and ionic steepest descent dynamics has been used to determine optimal surface structures. We have used a repeated slab geometry, each slab consisting of five layers of Ge atoms. On top of the first layer we have added the Pb (Sb) atoms. The bottom surface was saturated by hydrogen atoms. Two consecutive slabs were separated by an empty space 9.0 Å wide. The four topmost Ge layers of the slab and the Pb (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 Ge layers were allowed to relax) in selected configurations. The relaxed atomic coordi-

nates were almost unchanged. Most of the calculations were performed using a $c(4 \times 8)$ supercell with 16 atoms/layer. Due to the large size of our unit cell, only the electronic states at Γ have been included. For the (2×1) structure of Sb on Ge(100), the size of the unit cell was tested by optimizing the atomic positions using a smaller $p(\sqrt{3} \times \sqrt{3})$, and obtaining similar results. The wave functions have been expanded in plane waves with a kinetic energy cutoff $E_{cut} = 8$ Ry. We have used for Ge, Pb, and Sb norm-conserving pseudopotentials that include s and p nonlocal terms. They were treated within the Kleinman-Bylander scheme.[19] The Ge pseudopotentials have been extensively tested in previous calculations of bulk, liquid,[20] amorphous,[21] and the (111) surfaces of Ge at several temperatures.[22] The Pb pseudopotential has been used by Ancilloto, Selloni, and Car in a study of Pb on Ge(111) at several temperatures.[23] The Sb pseudopotential has been tested in the bulk, and in previous studies of the adsorption of Sb on Ge(111), Si(111), Ge(100), and Si(100), giving excellent results.[24–27] Other computational details are as in Ref. 24.

We have determined the optimum geometry of the $c(4 \times 8)$ structure, starting from an ideal Ge(100) surface covered by a $c(4 \times 8)$ arrangement of Pb adatoms. The initial configuration was similar to the model proposed by Quate *et al.* for Sn on Si(100). After a full relaxation of the atomic positions, we arrived at the structure shown in Fig. 1. It is formed by asymmetric Pb dimers arranged in chains, with periodicity $4a$ along the chains. Each chain consists of three rows of Pb dimers. Consecutive chains are separated by trenches (places where there are no Pb atoms). Since adjacent chains are 180° out of phase, the local order is $c(4 \times 8)$. Ge atoms located on one side of a trench are bonded to opposite Ge atoms across the trench. In this way each Ge atom has all its dangling bonds saturated, and the surface is very stable. This model was proposed by Yang *et al.* in their work of Pb on Ge(100).[16]

The calculated Pb-Pb dimer bond length is $d_{Pb\text{-}Pb} \sim 3.10$ Å, which is smaller than the bulk nearest-neighbor distance $d_{Pb\text{-}Pb} \sim 3.50$ Å. The Pb dimer is asymmetric: there is a vertical separation between the two atoms of $\Delta z \sim 0.81$ Å, yielding a buckling angle of $\sim 15°$. Pb-Ge bond lengths are $d_{Pb\text{-}Ge} \sim 2.80$ Å and $d_{Pb\text{-}Ge} \sim 2.74$ Å for the up and down adatom, respectively. They are also smaller than the sum of the Pauling covalent radii of ~ 2.98 Å. These are indications that due to the large size of the Pb atoms, the Pb-Pb and Pb-Ge bonds are highly compressed. The bond length between the first-layer Ge dimers is $d_{Ge\text{-}Ge} \sim 2.66$ Å. Even though the Pb-Pb and Pb-Ge bond lengths are almost the same for all dimers, it is found that dimers in the middle row (of the chains) are ~ 0.08 Å higher than dimers close to the trenches (see Fig. 1).

Similar results were found for the $c(4 \times 8)$ structure of Pb on Si(100). The calculated Pb-Pb dimer bond length is $d_{Pb\text{-}Pb} \sim 3.06$ Å. The Pb dimer is also asymmetric: there is a vertical separation between the two atoms of $\Delta z \sim 0.76$ Å, yielding a buckling angle of $\sim 14°$. Pb-Si bond lengths are $d_{Pb\text{-}Si} \sim 2.79$ Å and $d_{Pb\text{-}Si} \sim 2.69$ Å for the up and down adatom, respectively. The bond length between the first-layer Si dimers is $d_{Si\text{-}Si} \sim 2.49$ Å. It is also found that dimers in the middle row (of the chains) are ~ 0.09 Å higher than dimers close to the trenches.
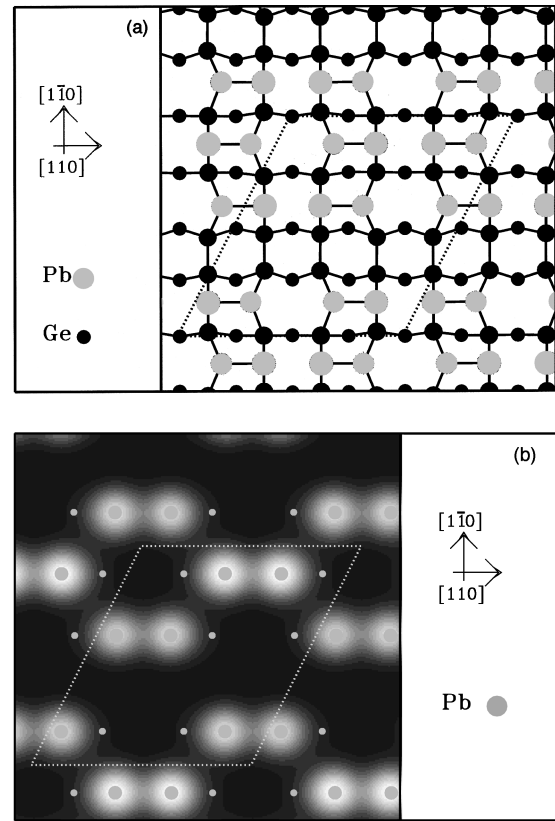

FIG. 1. (a) Top view of the atomic structure of the (100) surface of Ge with 0.75 of a Pb monolayer and $c(4 \times 8)$ symmetry. The unit cell used in the calculation is marked with dotted lines. Gray circles represent the 12 Pb atoms, while black circles represent Ge atoms. Bigger circles correspond to atoms closer to the surface. (b) Gray plots of the local density of states calculated at $E \sim -1.0$ eV. Gray circles represent the Pb atoms. Big and small circles correspond to the up and down atoms, respectively.

The mechanism of stabilization of these surfaces is similar to the (2×1) reconstruction of clean Si(100) and Ge(100): Pb has four valence electrons (the same as Si and Ge), two of the electrons are used in the bonds with Ge dangling bonds, and another in the formation of the Pb dimer. In this way each Pb atom of the dimer remains with one electron not engaged in any bond. To lower the energy, there is a charge transfer from the atom that moves down to the one that moves up.

In the clean Si(100) surface, dimers are flipping back and forth from two possible orientations of the dimers. Dabrowski and Scheffler[28] have shown that the energy barrier between the two configurations is very small: ~ 0.09 eV/dimer. In the $c(4 \times 8)$ structure, similar buckling vibration is not expected. In this case, the orientation of each Pb dimer is crucial to obtain the $c(4 \times 8)$ reconstruction. To test this idea further, we have calculated the energy barrier for one of the Pb dimers[29] to flip into the other orientation. We found a large barrier of ~ 0.5 eV/dimer, more than five times larger than in the case of clean Si(100).

Since most of the structural information about the $c(4 \times 8)$ surface comes from STM experiments, it is important to compare our results with them. We approximate a theoretical tunneling current density $j(\mathbf{r})$ by[30]
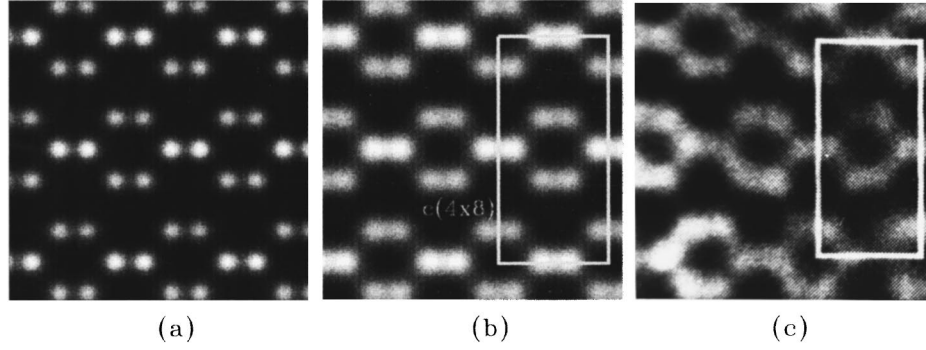
FIG. 2. (a) Gray plots of the local density of states calculated at $E \sim -1.0$ eV [same as in Fig. 1(b), but showing a larger area]. (b) Calculated results of (a) have been filtered out to mimic experimental conditions. (c) Filled states STM image of Si(100)$c(4 \times 8)$-Sn from Ref. 10.

$$j(r,V) \propto \int_{E_F - eV}^{E_F} \rho(r,E)dE, \qquad (1)$$

where

$$\rho(r,E) \equiv \sum_{n,\mathbf{k}} |\psi_{n,\mathbf{k}}(r)|^2 \delta(E_{n,\mathbf{k}} - E). \qquad (2)$$

Here $\rho(\mathbf{r},E)$ is the local density of states at the tip position $\mathbf{r} = (x,y,z)$, and the $\psi_{n,\mathbf{k}}(\mathbf{r})$ are the eigenstates of the surface with corresponding energy $E_{n,\mathbf{k}}$. We integrate the charge density of the $c(4 \times 8)$ structure of Pb on Ge(100) using Eq. (1) for $V = 1.0$ V and $z \sim 2$ Å. In the simplest approximation, this corresponds to the experimental procedure of probing surface states at a negative bias voltage of 1.0 V [similar results are found for Pb on Si(100)]. The results [Fig. 1(b)] show that the brightest features of the image originate from the Pb atoms that are buckled up. They correspond to the occupied dangling bond of these atoms. The agreement between theory and experiment[16] is good: in both cases the bright features come from the up atoms of the Pb dimers. In Fig. 2(a) we show the same density of states, without showing the Pb atoms, and extending the range of the figure. When comparing experimental and theoretical images, one should bear in mind that there are limits in the real STM resolution. To mimic this effect[31] we filter out the high-frequency Fourier components from the calculated current density shown in Fig. 2(a) to produce Fig. 2(b), which shows a very strong similarity to the experimental data.[16] To point out that our proposed structure for Ge(100)$c(4 \times 8)$-Pb could also be used to describe other surfaces with similar $c(4 \times 8)$ reconstructions, we present in Fig. 2(c) a STM image of Sn on Si(100).[10] It can be seen that the similarity between Figs. 2(b) and 2(c) is remarkable.

In order to check the stability of the $c(4 \times 8)$ compared with other phases, we have also performed calculations of a full monolayer of Pb on Ge(100). The final relaxed atomic configuration can be described as a distorted (2×1) surface. It also consists of Pb dimers. However, in the present case, the buckling angle of Pb dimers changes from row to row. This is probably a mechanism to release the strain produced when the extra four Pb atoms are introduced into the unit cell.

The relative stability of the two structures with different coverage can be determined from the Pb-chemical potential dependent surface formation energies:

$$\Omega(\mu) = E_{slab} - N_{Ge}\mu_{Ge,bulk} - N_{Pb}\mu_{Pb}, \qquad (3)$$

where E_{slab} is the total energy of the Pb-Ge system, N_{Ge} and N_{Pb} are the number of Ge and Pb atoms, $\mu_{Ge,bulk}$ is the energy per atom in bulk Ge, and μ_{Pb} is the Pb-chemical potential referred to that of Pb atoms in the bulk phase. The results are shown in Fig. 3(a). For negative values of μ_{Pb} the $c(4 \times 8)$ structure is always more stable than the (2×1). Under equilibrium conditions, only negative values of μ_{Pb} are allowed.

As mentioned in the introduction, the $c(4 \times 8)$ phase has to the best of our knowledge, never been observed for either group III or group V elements. However, it is interesting to
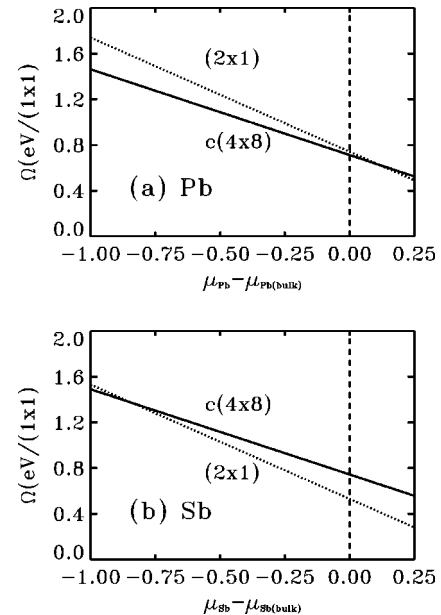

FIG. 3. (a) Surface formation energies as functions of the Pb chemical potential for the Ge(100)$c(4 \times 8)$-Pb and Ge(100)2×1-Pb. (b) Surface formation energies as functions of the Sb chemical potential for the Ge(100)$p(2 \times 4)$-Sb and Ge(100)2×1-Sb.
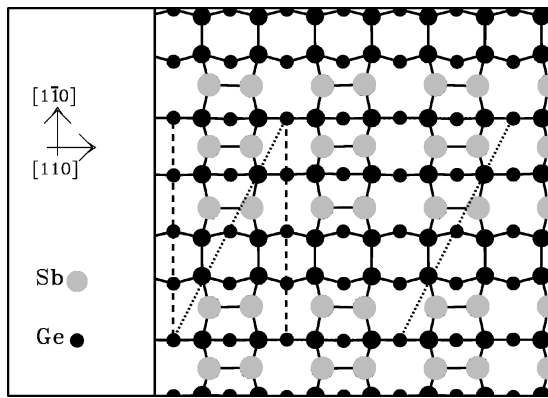
FIG. 4. Top view of the atomic structure of the (100) surface of Ge with 0.75 of a monolayer of Sb. The unit cell used in the calculation is marked with dotted lines. Gray circles represent the 12 Sb atoms, while black circles represent Ge atoms. Bigger circles correspond to atoms closer to the surface. Note that the periodicity is now $p(2 \times 4)$ (the unit cell is marked with dashed lines).

study the characteristics of the $c(4 \times 8)$ structure in those cases, and to check whether the (2×1) structure is indeed more stable.

A previous calculation of a monolayer of Sb on Ge(100) has shown that the Sb atoms form symmetric dimers on an almost unreconstructed Ge surface.[26] The Sb-Sb and the Sb-Ge bond lengths are $d_{\text{Sb-Sb}} \sim 2.95$ Å and $d_{\text{Sb-Ge}} \sim 2.62$ Å, respectively. The nearest-neighbor distance in bulk Sb is $d_{\text{Sb-Sb}} \sim 2.87$ Å and the sum of covalent Sb and Ge radius is $d_{\text{Sb-Ge}} \sim 2.62$ Å.

To obtain the $c(4 \times 8)$ reconstruction of Sb on Ge(100), we have optimized the atomic structure of the (100) surface of Ge covered by 0.75 of a Sb monolayer. The starting point of the relaxation was the $c(4 \times 8)$ structure of Pb on Ge(100). As discussed before, in this configuration the ad-dimers are buckled. At the end of the atomic optimization, the Sb atoms form fully symmetric dimers, as in the case of the (2×1) structure. Because the ad-dimers are not asymmetric anymore, the structure is no longer $c(4 \times 8)$, but has a smaller periodicity $p(2 \times 4)$, as seen in Fig. 4. The Sb-Sb bond length is $d_{\text{Sb-Sb}} \sim 2.91$ Å, similar to the (2×1) result. The Sb-Ge bond length is 2.70 Å for the dimers in the middle of the chain, and 2.75 Å for dimers close to the trench. They are larger than in the case of the (2×1) structure, indicating that the bonds are weaker. The distance between Ge atoms in the first layer is $d_{\text{Ge-Ge}} \sim 2.87$ Å, also showing that the bond between Ge dimers is weaker than in Pb on Ge(100).

In Fig. 3(b) we compare the formation energies of the (2×1) and $p(2 \times 4)$ structures for Sb on Ge(100). The (2×1) structure has a significantly lower surface energy than the $p(2 \times 4)$. Thus the $p(2 \times 4)$ structure could not be prepared under equilibrium conditions.

The main difference between Pb and Sb on Ge(100) is that Pb atoms form buckled dimers, while the Sb dimers are symmetric. This is due to the fact that Pb has four valence electrons and Sb five. It is quite natural that the same $c(4 \times 8)$ reconstruction occurs on Pb on Si(100) and Sn on Si(100) and Ge(100), but not in the growth of group III and V elements on Si and Ge(100).

In summary, we have performed a first-principles total-energy calculation of the $c(4 \times 8)$ structure of Pb on Ge(100). Our results show that the surface is formed by asymmetric Pb dimers, with a buckling angle of 15°. Calculations of the surface formation energy indicate that the $c(4 \times 8)$ is more stable than a structure with a full Pb monolayer. Opposite results were found for Sb on Ge(100), where the (2×1) structure is preferred over the $c(4 \times 8)$.

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