Scanning tunneling microscopy and *ab initio* calculations: $c(4\times 8)$ reconstructions of Pb on Si and Ge(001)

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(Received 2 November 2000; revised manuscript received 9 February 2001; published 14 June 2001)

The $c(4\times 8)$ reconstructions induced by Pb atoms on Si(001) and Ge(001) surfaces have been studied by scanning tunneling microscopy (STM) and first-principles total-energy calculations. Two different structures were found experimentally. In both cases, there is a coexistence of Pb and Si(Ge) dimers either in perpendicular and/or in parallel orientations. The $c(4\times 8)$ - α phase is similar to the structure previously reported for Pb on Si and Ge(001) and Sn on Si(001). It is formed by three rows of asymmetric Pb dimers forming chains along the $[110]$ direction, and it corresponds to a coverage of 0.75 monolayer (ML). In the second structure, the $c(4\times 8)$ -1 phase, the middle Pb dimers are replaced by Si(Ge) dimers resulting in a Pb coverage of 0.5 ML. The agreement between bias-dependent STM images and calculated local density of states for the two structures is excellent. Our calculations show that the $c(4\times 8)$ - α structure is generally the most stable configuration for Si and Ge surfaces covered by Pb. However, if there is a deficit of Pb atoms, the $c(4\times 8)$ -1 structure becomes more stable for Pb on Si(001).

DOI: 10.1103/PhysRevB.64.035304

PACS number(s): 68.35.Bs, 71.15.Mb

I. INTRODUCTION

The adsorption of thin metal overlayers on semiconductor surfaces is the subject of intense research, not only due to its technological applications but also for fundamental reasons. In particular, the adsorption of Pb on Si and Ge surfaces has attracted considerable interest over the past few years.^{1–16} Pb atoms show very low solubility in the Si(Ge) bulk environment, and the closely related systems Pb on Si and Pb on Ge are considered as prototype examples for abrupt metal-semiconductor interfaces.² Most investigations focused on lead-covered Si(111) and Ge(111) surfaces, where, depending on the exact coverage, heat treatment, and temperature, a variety of different two-dimensional (2D) phases have been found. The observation of low-temperature phase transitions and commensurate-incommensurate phase transitions demonstrates that these systems, although apparently rather simple, exhibit a variety of interesting physical phenomena.

Low-energy electron diffraction (LEED) experiments show that the phase diagram of Pb adsorbed Si(001) and Ge(001) surfaces is similarly rich in reconstructions.^{6,7} These results have been confirmed by a variety of other experimental techniques.^{8–16} When less than one monolayer of Pb is deposited on Ge(001) at room temperature, structures with (2×2) , (2×4) , $c(4\times 2)$, and $c(4\times 8)$ periodicities are observed. Similar (3×2) , (2×2) , and $c(4\times 8)$ reconstructions have been found for Pb on Si(001) in the submonolayer regime. The basic building blocks of all these structures are Pb dimers on a (partially) dimerized substrate layer.^{8,10–16}

In this paper, we report a detailed experimental and theoretical study of the $c(4\times 8)$ reconstruction that Pb forms on Si (Refs. 8 and 10) and Ge(001).^{11–14} The interest in this particular phase arises from the fact that it corresponds to the (001) surfaces of Si and Ge being totally covered with Pb

dimers. Other phases, such as the (2×2) also occurs in the adsorption of group-III metals on Si and Ge(001).^{19,20}

Two different structures, both having the $c(4\times 8)$ periodicity, have been found in our work. Based on the analysis of the experimental bias-dependent STM images and supported by *ab initio* pseudopotential density-functional calculations, we present models for each structure. They consist of chains of dimers along the $[110]$ direction. The $c(4\times 8)$ - α phase is similar to the structure previously reported for Sn on Si(001) (Refs. 17 and 18) and Pb on Si and Ge(001), and it corresponds to a coverage of 0.75 ML. The second $c(4\times 8)$ structure has never been reported previously and it consists of mixed Pb dimers and Si (Ge) dimers with a coverage of 0.5 ML [we will refer to this new reconstruction as the $c(4\times 8)$ light or $c(4\times 8)$ -1 phase]. Using first-principles total-energy calculations, we have studied the stability of these two phases.

II. METHOD

A. Experimental setup

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure less than 4×10^{-11} mbar. The UHV system is equipped with STM, low-energy electron diffraction (LEED), and reflection high-energy electron diffraction (RHEED). Polished Si(001) and Ge(001) wafers ($\sim 7\times 4\times 0.5$ mm³) were rinsed in pure methanol, loaded in the UHV chamber and out gassed by dc heating at temperatures up to 650 °C (Ge) and 900 °C (Si). Clean reconstructed Ge(001) surfaces were prepared by repeated cycles of sputtering with 500-eV Ar⁺ ions at a temperature of 500 °C and annealing at 650 °C, until a sharp (2×1) LEED pattern with a low background and modulated streaks indicating extended $c(4\times 2)$ domains were observed.

Clean Si(001)-(2×1) surfaces were achieved by repeated cycles of heating the substrates to above 1150 °C for some 10 s, quickly cooling down to 900 °C and holding for 15 min. Finally, the heating current was turned down over a 3-h period. Pb was evaporated from an effusion cell with a pyrolytic boron nitride crucible at a rate of $\sim 2.5 \times 10^{-3}$ ML/s, where one monolayer (1 ML) is equal to $6.78[6.24] \times 10^{14}$ atoms cm^{-2} for Si(001) [Ge(001)]. The effusion cell has been calibrated with a quartz microbalance and by counting the lead atom density observed in STM images of low-coverage Ge(111) $c(2 \times 8)$ -Pb reconstructed surfaces.³ Above 400 °C the temperature was measured with an optical pyrometer and below 400 °C the temperature was estimated from the heater power.

B. Theoretical method

The first-principles calculations have been performed within the local-density-functional theory, using the Car-Parrinello approach.²¹ We have used a repeated slab geometry, each slab consisting of five layers of 16 Si (Ge) atoms and a $c(4 \times 8)$ periodicity. This arrangement corresponds to 16 (1×1) unit cells. The bottom surface was saturated by hydrogen atoms in a dihydride structure. The Pb atoms were placed on top of the first Si layer. Two consecutive slabs were separated by an empty space 9.0 Å wide. The Pb adatoms and the four topmost Si (Ge) layers of the slab had full freedom to move. The fifth Si (Ge) layer and the H atoms were frozen in order to simulate a bulklike environment. Only the Γ point was sampled. This corresponds to 16 k points in the (1×1) surface Brillouin zone. This geometry was found to be adequate in a previous calculation of Pb on Si(001) for coverages less than 0.5 ML (Ref. 22) and Pb on Ge(001) for coverages of 0.5 and 0.75 ML (Refs. 23 and 24). The wave function was expanded in plane waves with kinetic energy cutoff $E_{\text{cut}} = 8$ Ry. We have used norm-conserving pseudopotentials that included s and p nonlocal terms. They were treated within the Kleinman-Bylander scheme.²⁵ A steepest-descent (SD) algorithm was used for electronic energy minimizations at fixed ionic positions. This was combined with a similar (SD) dynamics of the ions to determine the optimum surface structure.²⁶

III. RESULTS

Previous LEED and STM studies have shown that deposition of 0.5–1 ML of Sn on Si(001) at a temperature above 500 °C (Ref. 17) and Pb on Si and Ge(001) (Refs. 6–14) at room temperature results mainly in a $c(4 \times 8)$ superstructure. A $c(4 \times 8)$ structure can also be obtained by annealing (2×2) or $c(4 \times 2)$ reconstructed surfaces formed by Pb on Si and Ge(001) at low coverage. It will be shown in this section that the $c(4 \times 8)$ structures can be classified in two subspecies, namely the $c(4 \times 8)$ - α reconstruction and the $c(4 \times 8)$ -1 reconstruction.

A. The $c(4 \times 8)$ - α structure

Figures 1(a) and 1(b) are STM images representative of the $c(4 \times 8)$ - α structure. Both figures depict the same region

FIG. 1. STM images of 0.4 ML Pb on Ge(001) deposited at 200 °C. (a) Filled states, (b) empty states. Buckled germanium dimer rows (A) coexist with domains of the $c(4 \times 8)$ reconstruction (B). The $c(4 \times 8)$ periodicity is perturbed by antiphase domain boundaries (C) and irregular arrangements of the subunits (D). Scan area $150 \text{ Å} \times 150 \text{ Å}$; (a) $V_{\text{sample}} = -2.4 \text{ V}$, $I = 1.3 \text{ nA}$, (b) $V_{\text{sample}} = +1.2 \text{ V}$, $I = 0.5 \text{ nA}$.

of the surface and correspond to filled and empty states, respectively. The Ge(001) surface shown is covered with ~ 0.4 ML of Pb deposited at ~ 200 °C. The images extend over two Ge(001) terraces that are covered with a mixture of the $c(4 \times 2)$ and (2×2) buckled dimer reconstructions of clean Ge(001) (e.g., at A) coexisting with the Pb-induced $c(4 \times 8)$ - α reconstruction (e.g., at B). The $c(4 \times 8)$ - α domain size is rather small, and many defects such as antiphase domain boundaries (region C) and stacking faults (region D) can be observed. The surface is completely $c(4 \times 8)$ - α reconstructed at a Pb coverage of 0.75 ML. The corrugation along the chains of the $c(8 \times 4)$ - α structure is typically ~ 1.0 Å for occupied states and ~ 0.6 Å for empty states. The height difference between the region covered by the $c(4 \times 8)$ - α reconstruction and the Ge dimer rows is ~ 1.8 Å.

We have performed first-principles total-energy calculations to have a more quantitative description of the surface

FIG. 2. Top view of the atomic structure of the (001) surface of Si (Ge) with 0.75 ML of Pb having the $c(4 \times 8)-\alpha$ structure. The unit cell used in the calculation is marked by dotted lines, while a (4×8) cell is denoted with full lines. Gray circles represent the Pb atoms, while black circles represent substrate atoms. Larger circles correspond to atoms closer to the surface.

structure, and we have determined the optimum geometry of the $c(4 \times 8)-\alpha$ reconstruction of Pb on Ge(001) and Si(001). Preliminary results have been published previously.²⁴ Here, we give a complete description of the structural properties for both the $c(4 \times 8)$ -Ge(001)-Pb and the $c(4 \times 8)$ -Si(001)-Pb surfaces.

The initial configuration of our calculations was similar to the model proposed by Baski, Quate, and Nogami for Sn on Si(001).¹⁷ After fully relaxing the atomic positions, we have obtained the structure shown in Fig. 2. The surface is terminated by Pb dimers with a coverage of 0.75 ML, and forming a chain structure along the $[110]$ direction. Each chain is formed by three rows of asymmetric Pb dimers. Two consecutive dimers along and perpendicular to the chain have opposite orientations. Therefore, the periodicity is $4a$ [a being the lattice parameter of the clean unreconstructed Si or Ge(001) surface]. Each chain is separated from the next one by trenches where there are no Pb atoms. The trenches are energetically favorable and allow the larger Pb atoms to be accommodated on the smaller Si (Ge) substrate. There are two different kinds of Pb dimers: (a) those next to the trenches and (b) dimers in the middle of the chain. Although both of them have more or less the same bond length, dimers in the middle are higher than those next to a trench. The difference is ~ 0.09 and ~ 0.08 Å for Si and Ge, respectively. Since adjacent chains are 180° out of phase, the local order is $c(4 \times 8)$. Si (Ge) atoms located on one side of a trench are bonded to opposite Si (Ge) atoms across the trench. In this way each Si (Ge) atom has all dangling bonds saturated. In Tables I and II we have summarized the main structural parameters of the $c(4 \times 8)-\alpha$ structures formed by Pb on Si(001) and Ge(001) surfaces. We have also included calculated values of the Si(001) (2×2) -Pb and Ge(001) (2×2) -Pb structures. It can be observed that the structural parameters related to the Pb dimers are changed little in going from the (2×2) to the $c(4 \times 8)-\alpha$ reconstruction. The differences are

TABLE I. Calculated bond lengths and buckling amplitude (in Å) for the Pb/Si(001) system. The Pb and Si covalent radii are 1.44 and 1.18 Å, respectively. The Si bond length in the clean Si(001) $c(2 \times 4)$ structure is 2.24 Å.

	(2×2)	$c(4 \times 8)-\alpha$	$c(4 \times 8)-1$
Pb-Pb ad-dimer	3.13	3.06	3.09
Pb dimer Δz	0.70	0.76	0.69
Pb-Si (upper Pb)	2.80	2.79	2.82
Pb-Si (lower Pb)	2.74	2.69	2.73
Chain Si-Si dimer			2.27
Si dimer Δz			0.55
Substrate Si-Si dimer	2.40	2.49	2.50

slightly larger for Ge than for Si. In general, the structural parameters of the $c(4 \times 8)-\alpha$ structure are closer to the sum of covalent radii. For the (2×2) reconstruction, the Pb dimers are parallel to the Si (Ge) dimers. For the $c(4 \times 8)-\alpha$ phase, the Pb dimers are orthogonal to the Si (Ge) dimers. In both cases, the Si (Ge) dimers become weakened by the adsorption of the Pb dimers. This effect is larger in the $c(4 \times 8)-\alpha$ reconstruction.

The fact that the two atoms in the dimers do not have the same vertical position is not surprising. As in other similar cases this asymmetry can be correlated to the electronic structure: Pb has four valence electrons. Two of them saturate dangling bonds of the Si surface and another is used in the formation of the Pb—Pb bond. There is one remaining electron in each Pb atom of the dimer. To lower the total energy, there is a charge transfer from one atom (which is pushed down) to the other (which goes up). In this way all the dangling bonds are saturated and the surface is stable. This charge transfer is reflected in the experimental STM images. Filled (empty) states are located at the position of the higher (lower) Pb atoms. Figures 3(a) and 3(b) display an enlargement of the sample area shown in Figs. 1(a) and 1(b). The dual-polarity images have been corrected through piezoelectric drift to ensure that the outlined $c(4 \times 8)$ unit cells in the figures are located at the same positions of the sample surface. In Fig. 3(a) the chainlike structure of the $c(4 \times 8)$ reconstruction is clearly resolved at the atomic level. The corresponding empty state image of Fig. 3(b) also shows a

TABLE II. Calculated bond lengths and buckling amplitude (in Å) for the Pb/Ge(001) system. The Pb and Ge covalent radii are 1.44 and 1.23 Å, respectively.

	(2×2)	$c(4 \times 8)-\alpha$	$c(4 \times 8)-1$
Pb-Pb ad-dimer	3.16	3.10	3.12
Pb dimer Δz	0.67	0.81	0.70
Pb-Ge (upper Pb)	2.86	2.80	2.86
Pb-Ge (lower Pb)	2.78	2.74	2.76
Chain Ge-Ge			2.38
Ge dimer Δz			0.59
Substrate Ge-Ge dimer	2.53	2.66	2.65

FIG. 3. (a, b) Enlarged regions from Fig. 1 showing the (a) filled states and (b) empty states of the $c(4 \times 8)$ - α structure. The circles mark a $c(4 \times 8)$ -1 unit. The outlined (4×8) unit cell indicates the same location on the sample. (c, d) Gray plots of the local density of states calculated at $E \sim -1.0$ eV (c) and ~ 1.0 eV (d). A (4×8) unit cell is marked by full lines and it corresponds to the same location in both figures.

chain structure. However, the bright spots are shifted by $2a$ in the direction parallel to the chains and the chain elements look different.

To make a direct comparison between our calculated structure and the STM images, we approximate a theoretical tunneling current density $j(\mathbf{r})$ by²⁷

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

where

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

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 energies $E_{n, \mathbf{k}}$.

We integrate the charge density 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 surface bias voltage of 1.0 V. When comparing experimental and theoretical images, one should bear in mind that there are limits in the real STM resolution. To mimic this effect, we have filtered out the high-frequency Fourier components from the calculated current density. The agreement between theory and experiment is excellent. The results [Figs. 3(a) and 3(c)] show that the brightest features of the image originate from the Pb atoms that buckle upwards. They correspond to the occupied dangling bonds of these atoms. It can also be observed that the spots in the middle of the chains are slightly more intense than those close to a trench. This is due to the fact that dimers in the middle are at a slightly higher vertical position.

Using $V = -1.0$ V and $z \sim 2$ Å corresponds to the experimental procedure of probing surface states at a positive sur-

FIG. 4. Filled state STM image of a Pb-covered Si(001) surface obtained after deposition of 2 ML Pb at room temperature and heat treatment at 460 °C under desorption of Pb, showing the new kind of $c(4 \times 8)$ -1 reconstruction coexisting with (4×2) reconstructed areas. Scan area $150 \text{ \AA} \times 150 \text{ \AA}$, $V_{\text{sample}} = -2.0 \text{ V}$, $I = 0.6 \text{ nA}$.

face bias voltage of 1.0 V. The results [Figs. 3(b) and 3(d)] show that the brightest features of the images originate from the Pb atoms that are buckled down. The similarity between Figs. 3(b) and 3(d) is remarkable.

The chain structure of the $c(4 \times 8)$ reconstruction of Sn on Si(001) surfaces (Ref. 17) and of Pb on Si(001) (Refs. 8 and 10) and Ge(001) (Refs. 9 and 11) surfaces after room-temperature deposition without annealing look similar in the published STM images to the chain structure shown in Fig. 3(a). All six protrusions per unit cell have nearly the same height. Therefore, all these $c(4 \times 8)$ reconstructions correspond to the (4×8) - α structure.

B. The $c(4 \times 8)$ -1 structure

In the Pb-covered (001) surface of Ge, there are regions where the periodicity is $c(4 \times 8)$ but the structure is different from the one described in the last section. The highlighted circle in Figs. 3(a) and 3(b) indicate an example of such a structure: the middle dimer is less intense than those next to the trench. It is possible to obtain a surface covered mostly by this type of Pb-induced $c(4 \times 8)$ structure on Si(001) surfaces by annealing at temperatures above 450 °C. Figure 4 shows a STM image of a Si(001) sample covered with Pb atoms forming wide domains of the new $c(4 \times 8)$ -1 structure (e.g., at A). In the upper right corner (e.g., at B) a previously unreported structure with (4×2) periodicity is observed. The (4×2) structure will be described in detail elsewhere.

Figures 5(a) and 5(b) display an enlargement of the sample depicted in Fig. 4. The double-polarity images reveal occupied and unoccupied sample states for exactly the same area on the sample. In the occupied state image in Fig. 5(a) the structure of the $c(4 \times 8)$ -1 reconstruction is clearly visible. Figure 5(b) looks similar, but the protrusions are shifted $2a$ in the direction parallel to the chains and the individual

atoms are better resolved. Small units with the $c(4 \times 8)$ - α reconstruction indicated by cycles can be also observed.

The STM images can be explained by a structural model similar to that used for the $c(4 \times 8)$ - α structure, but with the middle Pb dimers of the chains replaced by Si (Ge) dimers. We have also performed first-principles total-energy calculations in order to determine the optimum geometry of the $c(4 \times 8)$ -1 reconstruction. After fully relaxing the atomic positions, we have obtained the structure shown in Fig. 6. The surface is terminated by Pb and Si (Ge) dimers with a Pb coverage of 0.5 ML, forming a chain structure along the $[110]$ direction. Each chain is formed by three rows of asymmetric dimers: the middle dimers are Si (Ge) dimers, while the others are Pb dimers.

In column 3 of Tables I and II we have summarized the averages (there is a small variation of the bond lengths depending on the position of the dimer) of the main structural parameters of the $c(4 \times 8)$ -1 reconstruction of Pb on Si and Ge(001) surfaces. Bond lengths of Pb atoms are similar to those of the $c(4 \times 8)$ - α structure. Here, the middle dimers are formed by Si (Ge) atoms, with bond lengths and buckling amplitudes similar to those of a clean Si(001) $c(2 \times 4)$ surface.

Pb up (down) atoms are $0.64 \text{ \AA}$ ($0.50 \text{ \AA}$) higher than Si up (down) atoms. This is one of the reasons why the middle dimers have less intensity in the STM images.

Si (Ge) atoms located one side of a trench are bonded to opposite Si (Ge) atoms across the trench, forming symmetric dimers. Therefore, in this structure there are two kinds of Si (Ge) dimers: those in the middle of the chain, which are parallel to the Pb dimers and part of the top layer, and those in the trenches between the chains, which are orthogonal to the Pb dimers and are part of the first substrate layer. Again, the substrate Si (Ge) dimers are weakened by the absorption of the Pb dimers.

For both Pb and Si dimers that form the chains, the asymmetry is correlated with the electronic structure, Pb and Si atoms have four valence electrons. They form bonds with three other atoms. Therefore there is a remaining electron in each atom of the dimer. To lower the energy, there is a charge transfer from one atom to the other. This charge transfer is reflected in the experimental STM images. Filled (empty) states are located at the position of the higher (lower) Pb atoms.

To make a direct comparison between our calculated structure and the STM images, we approximate the theoretical tunneling current density $j(\mathbf{r})$ using Eqs. (1) and (2). For occupied and empty states we use $V = +1$ and $V = -1$ V respectively. In both cases we have used $z \sim 2 \text{ \AA}$. Comparison between theory and experiment is excellent, as seen in Figs. 5(a)–5(d) for occupied and empty states.

The results in Figs. 5(a) and 5(c) show that the brightest features of the image originate from the Pb atoms that buckle upwards. They correspond to the occupied dangling bonds of these atoms. In both experimental and theoretical images, there are very weak spots in the middle of the chain, originating from the Si atoms.

The results of Fig. 5(b) and 5(d) show that the brightest features of the image originate from the Pb atoms that buckle

FIG. 5. (a, b) High-resolution images showing the filled states (a) and empty states (b) of the $c(4 \times 8)$ -1 structure. The circles mark a $c(4 \times 8)$ - α unit. The outlined (4×8) unit cell indicate the same location on the sample. Sample area $60 \text{ \AA} \times 60 \text{ \AA}$, $U_{\text{sample}} = -2.0 \text{ V}$ (a), 2.0 V (b), $I = 0.6 \text{ nA}$. (c, d) Gray plots of the local density of states calculated at $E \sim -1.0 \text{ eV}$ (c) and $\sim 1.0 \text{ eV}$ (d). A (4×8) unit cell is marked by full lines and it corresponds to the same location in both figures.

downwards. In this case, the down Si atoms cannot be observed. This is due to two reasons: (i) The Si atoms are at a lower position with respect to the Pb atoms. In the case of the down Si atom, it is $\sim 1.18 \text{ \AA}$ below the up Pb atom. (ii) The empty state of the lower Pb atom is at a high position; it is close to the position of the filled state (despite the difference in height between the Pb atoms). The maximum contribution of the local density of states (LDOS) from the empty state around the Si atom is $1.18 \text{ \AA}$ below the maximum of the contribution due to the Pb atom, and therefore cannot be seen in the calculated LDOS image. Experimentally, the Si down atom cannot be observed in the STM image either. There is some intensity around the position of the up Si atom. This is an indication that the charge transfer from the down to the up atom is not complete, as in other similar systems.²⁸

C. Energetics of the $c(4 \times 8)$ structures

To compare the energetics of structures having different coverages, we calculate the chemical potential dependent surface formation energy of each configuration. It is defined as

$$\Omega(\mu_{\text{Pb}}) = E_{\text{slab}} - n_{\text{Si}}\mu_{\text{Si(bulk)}} - n_{\text{Pb}}\mu_{\text{Pb}}, \quad (3)$$

where E_{slab} is the total energy of a given slab configuration, n_{Si} and n_{Pb} are the number of Si and Pb atoms, respectively, $\mu_{\text{Si(bulk)}}$ is the energy per atom in bulk Si and μ_{Pb} is the Pb chemical potential. Under equilibrium conditions, the maximum possible value for μ_{Pb} is equal to the chemical potential of Pb in the bulk phase. Our results are summarized in Fig. 7(a) which shows that the two $c(4 \times 8)$ structures are stable phases. At $\mu_{\text{Pb}} = \mu_{\text{Pb(bulk)}}$ the energy of the $c(4 \times 8)$ - α is

FIG. 6. Top view of the atomic structure of the (001) surface of Si (Ge) with 0.5 ML of Pb with the $c(4 \times 8)$ -1 structure. The unit cell used in the calculation is marked by dotted lines, while a (4×8) cell is denoted with full lines. Gray circles represent the Pb atoms, while black circles represent Si (Ge) atoms. Larger circles correspond to atoms closer to the surface.

0.11 eV (1×1) lower than that of the $c(4 \times 8)$ -1 structure. This result indicates that at full Pb coverage, the $c(4 \times 8)$ - α structure is formed, in good agreement with our experimental results.

Figure 7 also shows that under poor Pb conditions, the $c(4 \times 8)$ -1 structure becomes more stable. This is also in agreement with experiments that show that the $c(4 \times 8)$ -1 reconstruction is obtained after desorbing Pb atoms at high temperature. This is an indication that if there is a deficit of Pb atoms, the $c(4 \times 8)$ -1 phase is formed on Si(001) surfaces.

Similar results are found for Pb on Ge(001) as shown in Fig. 7(b). At full coverage, the $c(4 \times 8)$ - α reconstruction is also the most stable configuration. Figure 7(b) seems to indicate that the $c(4 \times 8)$ -1 structure could also be formed after desorbing Pb atoms at high temperature. However, our experiments show that annealing Ge(001) samples in the Pb coverage range of 0.2–1 ML at temperatures above 300 °C results in completely different structures, namely, the rough phase and the (1×5) structure,¹⁴ which are not included in this work.

IV. SUMMARY

The $c(4 \times 8)$ phases of Pb on Si(001) and Ge(001) have been studied in detail with STM and first-principles total-energy calculations. Two different structures having the $c(4 \times 8)$ periodicity were found in our work: the $c(4$

FIG. 7. Chemical-potential-dependent surface formation energies for the $c(4 \times 8)$ - α , $c(4 \times 8)$ -1, and (2×2) reconstruction of Pb on (a) the Si(001) surface and (b) the Ge(001) surface.

$\times 8)$ - α and the $c(4 \times 8)$ -1. The geometrical structure of the $c(4 \times 8)$ - α reconstruction can be described by a structural model with 0.75-ML coverage consisting of triple rows of Pb dimers. Half of the Ge substrate dimers are broken and half of them become symmetric and perpendicular to the Pb dimers. In the second structure, the $c(4 \times 8)$ -1 phase, the middle Pb dimers of the chains are replaced by Si (Ge) dimers, resulting in a Pb coverage of 0.5 ML. Our calculations show that the $c(4 \times 8)$ - α reconstruction is the most stable structure for Si and Ge surfaces covered by Pb. However, if there are not enough Pb atoms, the $c(4 \times 8)$ -1 structure becomes more stable in the case of Pb on Si(001), but not in the case of Ge(001). The agreement between the calculated LDOS images and the experimental STM images for occupied and empty states is excellent for both structures.

ACKNOWLEDGMENTS

Calculations were performed at the Supercomputing Center DGSCA-UNAM. N.T. thanks Dr. J. A. Rodriguez for helpful conversations and DGAPA Project. No. IN119498, and CONACyT Project No. 27531-E for partial support. The financial support of the Volkswagen Stiftung under Project No. I 65 092 and the BMBF under Project No. 05 622GUA 1 is gratefully acknowledged.

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