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First-principles calculations of the atomic structure of the In-induced Si(001)-(4×3) reconstruction

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Using first-principles total-energy calculations, we have studied the atomic structure of the indium-induced Si(001)-(4×3) reconstruction. Three different models were considered. Our results indicate that the pyramidlike reconstruction proposed by Bunk *et al.* [Appl. Surf. Sci. 123/124, 104 (1998)] is more stable than the modulated (4×1) model of Zotov *et al.* [Phys. Rev. B 57, 12 492 (1998)], and the structure with seven In atoms/cell proposed by Saranin *et al.* [Phys. Rev. B 60, 14 372 (1999)]. Simulated scanning tunneling microscopy (STM) images based on the model of Bunk *et al.* are in better agreement with STM experiments than those based on the model of Zotov *et al.* An optimized structure with seven In atoms/cell is not compatible with STM experiments. These results strongly support pyramidlike structure of Bunk *et al.* to explain the Si(001)-(4×3)-In reconstruction.

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I. INTRODUCTION

When less than a monolayer of In is deposited onto a clean Si(001) surface, several superstructures have been observed depending on the In coverage and the substrate temperature.[1–13] For example, In deposition onto the Si(001) surface held at a temperature below 150 °C results in the formation of (2×3), (2×5), and (2×2) phases at In coverages of 0.3, 0.4, and 0.5 monolayer (ML), respectively.[2,5] The atomic structure of these reconstructions haven been determined conclusively, and it is well known that they all consist of symmetric In dimers adsorbed parallel and in the trenches between Si dimers. A completely different result occurs at high-temperature deposition, or when the surface is annealed: a (4×3) reconstruction is formed with an In coverage of 0.5 ML.[2–5,7–13] Although this reconstruction has been studied by several groups using different experimental techniques, the atomic structure of this phase is still the topic of some controversy. Scanning tunneling microscopy (STM) experiments by Baski *et al.*[2], by Li *et al.*,[4] and by Steele *et al.*[3] did not provide images with atomic resolution of In adatom locations. However, they gave certain restrictions for possible structures of the (4×3) reconstruction. Steele *et al.* proposed a model in which In atoms occupy two kinds of sites: adatom and substitutional.[7] They used it to fit their impact collision ion scattering spectroscopy data (ICISS). Yeom *et al.*, using high-resolution core-level photoelectron spectroscopy (CLPS),[8] and Krausch *et al.* using perturbed $\gamma\gamma$ angular correlation experiments (PAC),[9] compared the (4×3) and the (2×2) structures. They found that the two phases were very different and therefore excluded any model with In dimers for the (4×3) reconstruction. Krausch *et al.* found that In atoms occupy a variety of quite similar, however, somewhat different adsorption sites.[9] Yeom *et al.* also found that there are two kinds of Si atoms with different chemical and structural environments in the (4×3) unit cell and a single one for In.[8]

Based on these results, and new experiments using STM, low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES), Zotov *et al.* proposed a model for the Si(001)-(4×3)-In reconstruction consisting of three (4×1) building blocks, with a missing double-row structure of the substrate.[10,11] Each (4×1) subunit was formed by a silicon dimer and two indium atoms saturating all remaining dangling bonds. The (4×3) periodicity came from a modulation of the (4×1) building blocks. However, this model was found to be incompatible with surface x-ray diffraction experiments.[12,13] Instead, Bunk *et al.* proposed a pyramidlike reconstruction formed by In-Si dimers and a central In-Si-In trimer.[12,13] Very recently, Saranin *et al.*[15] claimed that the number of In atoms in the unit cell was seven, and therefore, they modified the Zotov *et al.* model by placing an extra In atom in the middle of the cell. Shimomura *et al.*[16] have pointed out that the semiconductor nature of the (4×3) reconstruction implies that the number of In atoms in the unit cell should be even, and therefore a model with seven indium atoms cannot be correct. Their x-ray photoelectron diffraction experiment favored instead the pyramidlike reconstruction.

The purpose of this article is to study the atomic structure of the (4×3) reconstruction. In particular, we have optimized the atomic positions according with the models of Zotov *et al.*, Saranin *et al.*, and Bunk *et al.*

It is found that the Saranin *et al.* structure is not stable. The seventh In atom, located originally in a twofold position, prefers to bind with four Si atoms. In this way, the structure of Saranin *et al.* is not compatible with STM experiments. Moreover, we have found that the pyramidlike structure proposed by Bunk *et al.* is the most stable among the three models. We have also considered other structures with fewer Si atoms, including one in which the topmost Si atom is replaced by an In atom. None of them were found to be more stable than the Bunk *et al.* model. Also, the calculated local density of states based on the Bunk *et al.* structure are in good agreement with STM experiments, while images based on the Zotov *et al.* model are not. These results strongly support the Bunk *et al.* model for the Si(001)-(4×3)-In surface.

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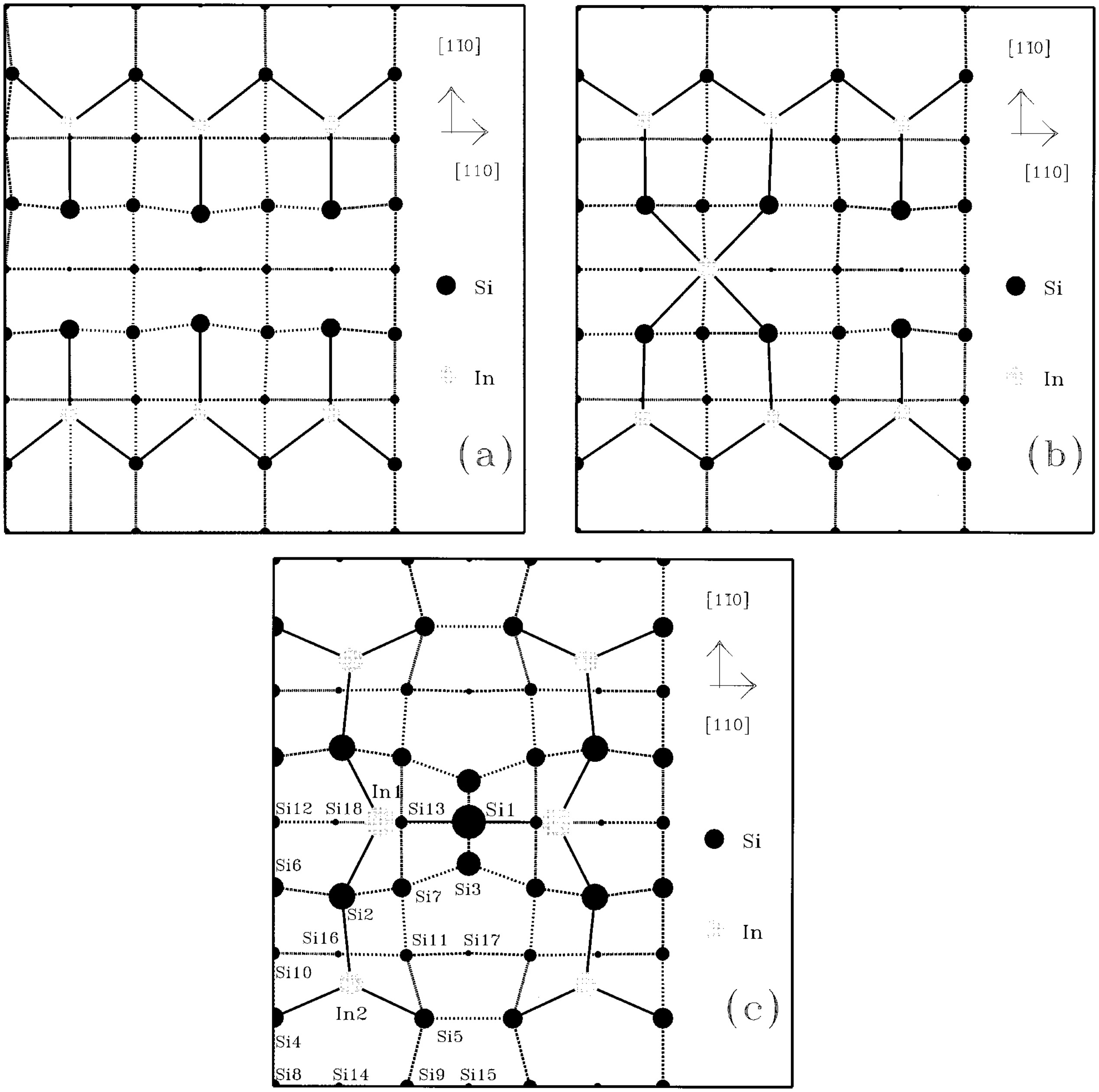

FIG. 1. Top view of the fully relaxed atomic structure of the In-covered (001) surface and (4×3) symmetry. Gray circles represent the six In atoms, while black circles represent In atoms. Bigger circles correspond to atoms closer to the surface. (a) Results obtained using the Zotov *et al.* model. (b) Results obtained using the Saranin *et al.* model. (c) Results obtained using the Bunk *et al.* model.

II. METHOD

Calculations have been performed within the Car-Parrinello scheme.[14] A combined electronic and ionic steepest descent dynamics has been used to determine optimal surface structures. Two different slab geometries were used, both of them having an in-plane (4×3) supercell with 12 atoms/layer. In the first one, the slab consisted of seven full layers of Si atoms. On top of the first layer we have added a mixed layer of Si and In atoms. The bottom surface was saturated by hydrogen atoms. Two consecutive slabs were separated by an empty space 9.0 Å wide. The six topmost layers of the slab were given full freedom to move, while the two deepest Si layers and the H atoms were held fixed at ideal positions in order to simulate a bulklike termination. In order to check the size of the cell, a second slab geometry was also used. It consisted of ten layers of atoms with two surfaces. The two middle layers were frozen in order to simulate a bulklike environment. Similar results were found. The relaxed atomic coordinates were almost unchanged and energy differences were less than 0.04 eV/(1×1) cell. Due to the large size of our unit cell, only the electronic states at Γ have been included. The wave functions have been expanded in plane waves with a kinetic energy cutoff $E_{\mathrm{cut}}=8$ and 10 Ry. Here, we present results obtained with the 10 Ry energy cutoff. We have used for Si and In norm-conserving pseudopotentials. They were constructed using the scheme of

Hammann, Schluter, and Chiang[18] and treated following the method of Kleinman and Bylander.[17] The *d* potential has been used as the local one, and we have included *s* and *p* nonlocal terms. The pseudopotentials have been extensively tested in previous calculations of similar systems.[19–21] Other computational details are as given in Ref. 20. The calculations correspond to zero temperature. Although experimentally the surface is created at high temperature (or annealed at high temperature), the measurements are obtained at room temperature. Since there are no phase transitions between 0 K and room temperature, the differences in the enthalpies do not change and the comparison between theory at 0 K and experiment at room temperature is meaningful.

III. MODELS OF ZOTOV *et al.*, SARANIN *et al.*, AND BUNK *et al.*

We have first determined the optimum geometry of the (4×3) structure, according to the model of Zotov *et al.* The starting point of the calculation was an unreconstructed Si(001) surface. On top of the first layer, we have placed six Si and six In atoms, having a (4×1) periodicity. The Si atoms were placed forming symmetric Si dimers. After a full relaxation of the atomic positions, we find the structure shown in Fig. 1(a). Indium atoms in the middle of the unit cell are slightly higher than those at the edges by ~0.04 Å. Instead Si atoms in the middle are lower than those in the edges by ~0.14 Å. In this way, the overall periodicity is no longer (4×1) but (4×3). In the final configuration, the Si dimers are broken, and therefore, there are six dangling bonds per unit cell.

To consider the Saranin *et al.* model, an additional In atom was place in the middle of the (4×3) cell. This configuration is not the most stable with seven In atoms per unit cell. Instead, we have obtained the structure shown in Fig. 1(b). The seventh In atom, located in a twofold position in the Saranin *et al.* model, prefers to bind with four Si atoms. Here, we have to point out that this structure is not compatible with STM experiments.

We have also determined the optimum geometry of the (4×3) structure, according to the Bunk *et al.* model. Again, we have started the calculation with an unreconstructed Si(001) surface. On top of the first layer, we have placed six Si and six In atoms forming mixed Si-In dimers. An additional Si atom is placed on top, so the In-Si-In trimer is formed. After a full relaxation of the atomic positions, we found the structure shown in Fig. 1(c). A detailed description of the atomic positions is given in the following section.

Since the three structures contain a different number of atoms, we cannot compare their total energies directly. Instead, we have to use the surface formation energy. Assuming that the slab is in thermal equilibrium with a Si and an In crystal, acting as reservoirs of Si and In atoms, the surface formation energy is defined as

$$\Omega = E_{\mathrm{slab}}(N_{\mathrm{Si}},N_{\mathrm{In}}) - N_{\mathrm{Si}}\mu_{\mathrm{Si,bulk}} - N_{\mathrm{In}}\mu_{\mathrm{In,bulk}},$$

where $E_{\mathrm{slab}}(N_{\mathrm{Si}},N_{\mathrm{In}})$ is the total energy of the Si-In system, N_{Si} and N_{In} are the number of Si and In atoms, $\mu_{\mathrm{Si,bulk}}$ and $\mu_{\mathrm{In,bulk}}$ are the energies per atom in bulk Si and In, respectively. It is found that indeed, the Saranin *et al.* model is more stable than the Zotov *et al.* model by ~0.9 eV/[(4×3) cell]. However the Bunk *et al.* structure has the lowest surface formation energy. Its surface energy is lower than the Zotov *et al.* energy by ~3.8 eV/[(4×3) cell].

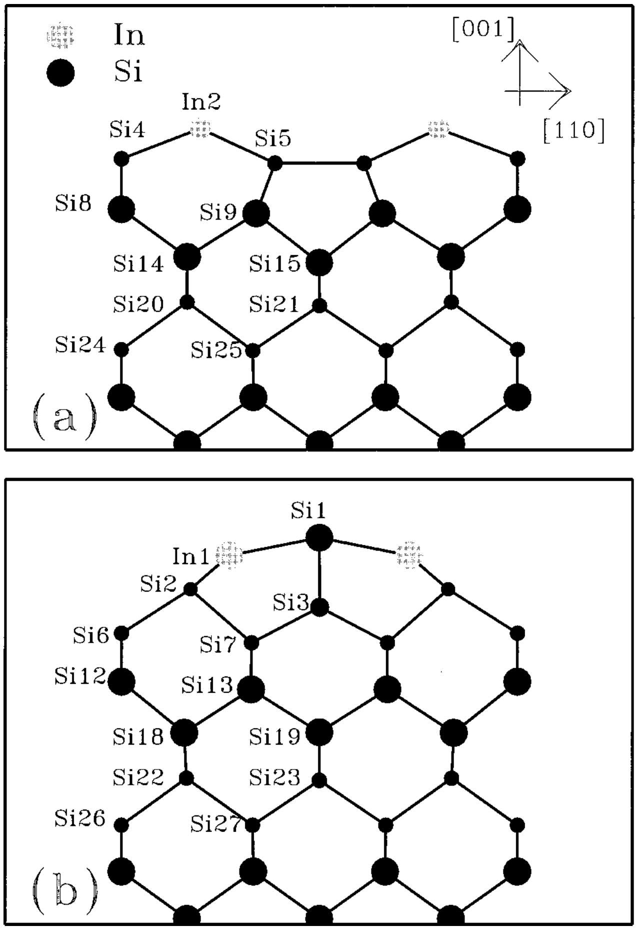

FIG. 2. Side view of the (4×3) reconstruction that In induces on Si(001). (a) The cut is from $y=0.0$ to $y=0.9$ relative to the unit cell in Fig. 1(b). (b) The cut is form $y=1.4a$ to $y=2.0a$.

IV. ATOMIC CONFIGURATION OF THE (4×3) STRUCTURE

In this section, we give a detailed description of the structural properties of the optimized (4×3) structure, according to the Bunk *et al.* model. In the following, we use LEED coordinates with $a=\frac{1}{2}[110]_{\mathrm{cubic}}$, $b=\frac{1}{2}[-110]_{\mathrm{cubic}}$, and $c=[001]_{\mathrm{cubic}}$. The cubic coordinates are in units of the bulk Si lattice constant $a_{\mathrm{Si}}=5.43$ Å. $|a|=|b|=3.84$ Å and $|c|=5.43$ Å. As mentioned before, Fig. 1(b) shows a top view of the fully optimized atomic structure. Figure 2(a) and 2(b) show two different side views of the surface. In Fig. 2(a) the cut is from $y=0.0$ to $y=0.9a$, relative to the unit cell shown in Fig. 1(b), while in Fig. 2(b) the cut is from $y=1.4a$ to $y=2.0a$. The *x* axis corresponds to the [110] direction, while the *z* axis correspond to the [001] direction. The atomic positions of the first six Si layers, the mixed Si, In layer, and the topmost Si adatom are given in Tables I and II, together

TABLE I. Calculated and experimental (Ref. 12) atomic positions in the In-induced Si(001)-(4×3) reconstruction. LEED coordinates are used. Layers 1–4.

Atom number	Calc. (x,y,z) coordinates	Expt. (x,y,z) coordinates
Si1	1.50, 2.00, 0.26	1.50, 2.00, 0.23
In1	0.82, 2.00, 0.17	0.72, 2.00, 0.20
In2	0.60, 0.78, −0.08	0.58, 0.73, −0.06
Si2	0.53, 1.44, −0.01	0.51, 1.44, −0.08
Si3	1.50, 1.69, −0.11	1.50, 1.67, −0.09
Si4	0.00, 0.52, −0.24	0.00, 0.52, −0.23
Si5	1.16, 0.51, −0.26	1.21, 0.52, −0.25
Si6	0.00, 1.51, −0.24	0.00, 1.48, −0.21
Si7	0.99, 1.51, −0.30	1.02, 1.52, −0.32
Si8	0.00, 0.00, −0.47	0.00, 0.00, −0.45
Si9	1.03, 0.00, −0.49	1.06, 0.00, −0.47
Si10	0.00, 1.01, −0.50	0.00, 0.98, −0.50
Si11	1.02, 0.99, −0.53	1.06, 0.98, −0.52
Si12	0.00, 2.00, −0.50	0.00, 2.00, −0.45
Si13	0.98, 2.00, −0.54	1.00, 2.00, −0.57
Si14	0.50, 0.00, −0.73	0.52, 0.00, −0.71
Si15	1.50, 0.00, −0.76	1.50, 0.01, −0.77
Si16	0.50, 1.00, −0.76	0.52, 0.99, −0.74
Si17	1.50, 1.01, −0.79	1.50, 1.01, −0.80
Si18	0.48, 2.00, −0.77	0.48, 2.00, −0.74

with experimental positions from X-ray diffraction[12]. In agreement with experiment, our calculation show the existence of considerable relaxations down to the sixth layer. In tables I and II, we can observe that in general, theory and experiment show similar trends. Indium atoms (In1) move towards the central Si1 atom. The same happens to Si3 atoms that move in the y-directions and form a dimer. Angles formed by the central Si1 atom with its neighbors are all equal, $\sim 80°$. Experimental values are 74°, 87°, 87°, and 74°. There are some noticeable differences between the calculated and experimental atomic positions, in particular, those related to the In-Si-In trimer. In Table III we show the theoretical and experimental bond lengths between some of the surface atoms. It can be observed that theoretical bond lengths are very close to the sum of covalent radii of the individual atoms. Instead, experimental bond lengths are quite large (with the exception of In2-Si4), in particular the bond length between atoms Si1 and In1, indicating that the bonds are highly stretched.

TABLE II. Calculated and experimental (Ref. 12) atomic positions in the In-induced Si(001)-(4×3) reconstruction. LEED coordinates are used. Layers 6 and 7.

Atom	Calc. (x,y,z) coordinates	Expt. (x,y,z) coordinates
Si19	1.50, 2.00, −0.77	1.50, 2.00, −0.80
Si20	0.50, 0.49, −0.99	0.53, 0.48, −0.99
Si21	1.50, 0.50, −1.01	1.50, 0.49, −1.02
Si22	0.50, 1.50, −1.01	0.49, 1.49, −0.99
Si23	1.50, 1.51, −1.02	1.50, 1.49, −1.04
Si24	0.00, 0.50, −1.25	0.00, 0.48, −1.23
Si25	0.99, 0.50, −1.25	1.00, 0.49, −1.25
Si26	0.00, 1.50, −1.26	0.00, 1.50, −1.25
Si27	0.99, 1.50, −1.26	0.98, 1.51, −1.26

TABLE III. Calculated and experimental (Ref. 12, in parenthesis from Ref. 16) bond lengths in the In-induced Si(001)-(4×3) reconstruction.

Atoms	Calc. bond length (Å)	Expt. bond length(Å)	Sum of covalent radii (Å)
Si1-In1	2.66	3.0 (3.0)	2.62
Si1-Si3	2.34	2.28 (2.4)	2.35
In1-Si2	2.61	2.75 (3.0)	2.62
In2-Si2	2.57	2.74 (3.0)	2.62
In2-Si4	2.66	2.54 (3.0)	2.62
In2-Si5	2.58	2.75 (3.0)	2.62

V. LOCAL DENSITY OF STATES AND STM IMAGES

Since all Zotov *et al.*, Saranin *et al.*, and Bunk *et al.* models were proposed based on STM images, it is important to compare our results with STM experiments. We approximate a theoretical tunneling current density $j(\mathbf{r})$ by[22]

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

where

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

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 two different models of the In-induced (4×3) reconstruction of Si(001) using the above equation with $z\sim 2$ Å $V=-2.0$,1.0, and 2.0 V. In the simplest approximation, this corresponds to the experimental procedure of probing surface states at a negative bias voltage of 2.0 V and positive bias voltages of 1.0 and 2.0 V, respectively. Figures 3 and 4 correspond to structures based on the Zotov *et al.* and Bunk *et al.* modes, respectively. We do not present images using the Saranin *et al.* model, since its optimized structure is not compatible with STM experiments.

In Fig. 3(a), the brightest features correspond to Si atoms. As mentioned before, our calculations show that Si atoms in the middle of the unit cell are at lower vertical positions than those at the edges. This difference can also be observed in the simulated STM images: one pair of spots are less intense than the other two pairs. Similar results are shown for empty states at low voltages. As seen in Fig. 3(b), the main features again correspond to Si atoms. Increasing the voltage, our simulated STM image now shows that the brightest features come from In atoms, but Si atoms can still be observed.

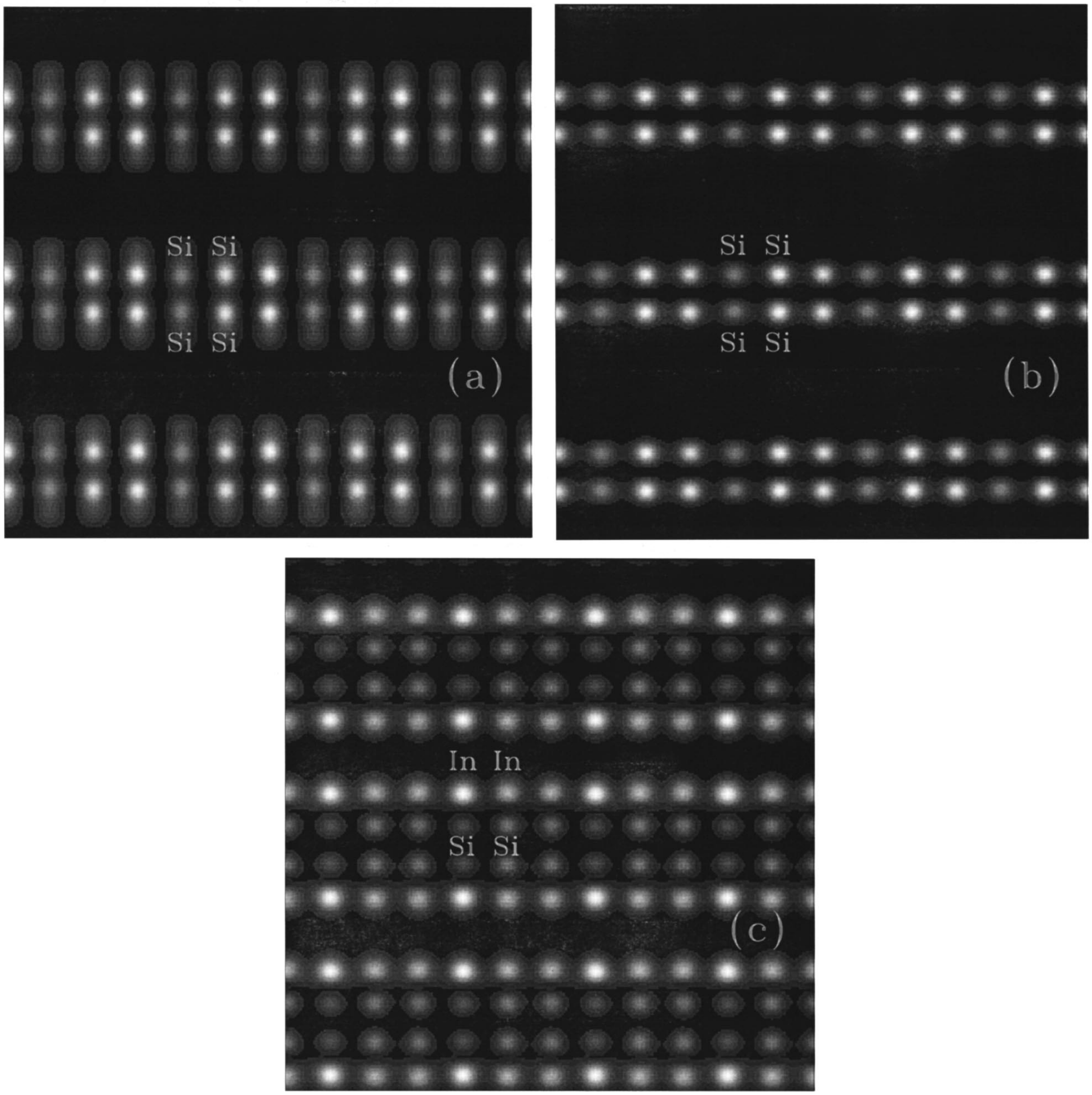

FIG. 3. (a) Gray plots of the local density of states calculated using the Zotov *et al.* model and (a) $E\sim-2.0$ eV, (b) $E\sim1.0$ eV, and (c) $E\sim2.0$ eV.

Again the intensity of the spots varies from one (4×1) subunit to another. Comparing Fig. 3 with experimental STM images, we can see that they are different. Therefore our calculations do not support the Zotov *et al.* model for the In-induced (4×3) reconstruction of Si(001).

We now come to the point of whether the Bunk *et al.* model can explain the STM investigations by Zotov *et al*. In Fig. 3, we plot the simulated STM images for three different voltages. Figure 4(a) corresponds to the filled states at $V=-2.0$ V. The bright features comes from the middle Si adatom. Figure 4(b) show the calculated empty state image obtained at $E=1$ eV. There are three protrusions corresponding to the middle Si atom and two of the In atoms. In our image, the Si atom appears slightly more intense than the In atoms. At a lower voltage, the image (not shown) is very similar to the occupied state image and only the Si atom can be observed. Increasing the energy to $E=2.0$ eV, the asymmetry in the three spots is reversed, and now In atoms become more intense. These theoretical images are in good agreement with the experimental work of Zotov *et al*. A filled state STM image at $V=-1$ V shows a single protrusion in each (4×3) unit cell. An empty state STM image at $V=0.7$ V shows three protrusions along the three periodicity, and at $V=2$ V only two of them can be observed.

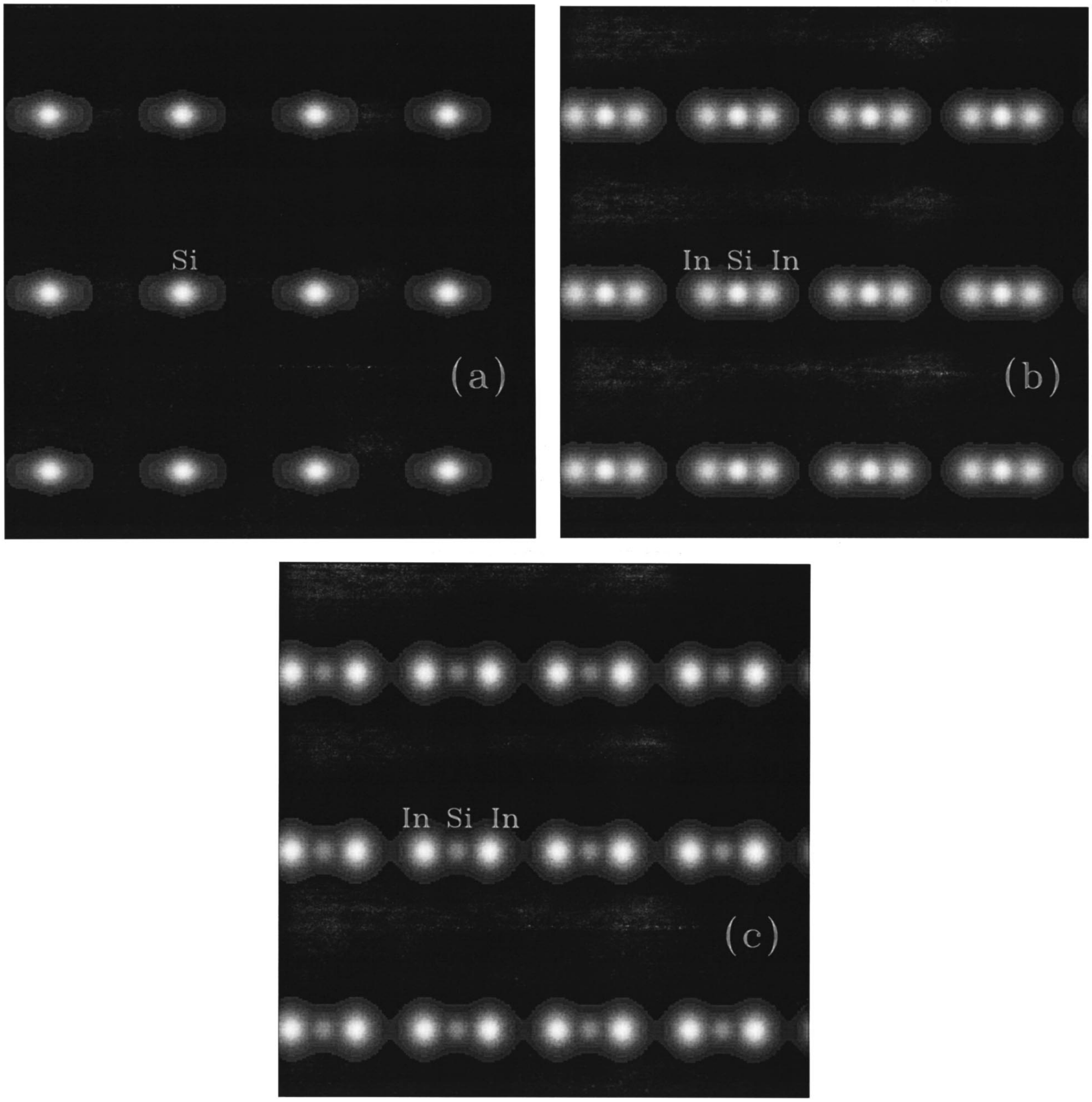

FIG. 4. (a) Gray plots of the local density of states calculated using the Bunk *et al.* model and (a) $E \sim -2.0$ eV, (b) $E \sim 1.0$ eV, and (c) $E \sim 2.0$ eV.

VI. CONCLUSIONS

Using first-principles total-energy calculations, we have studied the In-induced Si(001)-(4×3) reconstruction. In particular, we have optimized the atomic structure of the surface according to three different models: the modulated (4×1) structure proposed by Zotov *et al.*, the Saranin *et al.* model with seven In atoms, and the pyramidlike reconstruction proposed by Bunk *et al*. It was found that the original model of Saranin *et al.* model was not stable, and the optimized structure was not compatible with STM experiments. Moreover, our calculations show that the surface formation energy of the structure proposed by Bunk *et al.* is lower than those of the structures of Zotov *et al.* and Saranin *et al.* Also, the calculated local density of states based on the Bunk *et al.* structure are in better agreement with experimental STM images than those based on the Zotov *et al.* model. These results strongly support the Bunk *et al.* model for the Si(001)$\times(4\times3)$-In surface phase.

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