Atomic and electronic structure of the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface reexamined using first-principles calculations

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Abstract

We have reexamined the atomic and electronic structures of the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface using first-principles calculations within the local density functional approach. First, we found that a discrepancy among previous first-principles studies concerning the honeycomb-chained-triangle (HCT) model, which was believed to describe the structure of the surface, can be attributed to the difference in the structural parameters adopted in the calculations. Second, we have confirmed that the recently proposed inequivalent triangle (IET) model, where the positions of the Ag atoms are distorted a little from those in the HCT, is energetically more stable than the HCT one. We have also examined several other models that have distortions similar to the IET one. The results suggest that at room temperature the surface does not stay in the HCT configuration, but fluctuates between various configurations. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Properties of metal–semiconductor interfaces and metal-adsorbed semiconductor surfaces have attracted much attention in both technological and scientific aspects. From the technological point of view, the effects of such surfaces and interfaces on device functions become more significant as the size of semiconductor devices decreases. From the scientific point of view, the microscopic origin of the so-called Schottky barrier, which often appears at metal–semiconductor interfaces, has not been fully understood yet, for example. In this context, metal-adsorbed semiconductor surfaces have been investigated extensively (see, for example, Ref. [1]). In particular, Ag-adsorbed Si surfaces have attracted much attention, because these two components do not form silicides and thus their interfaces are expected to be sharp.

Among Ag-adsorbed Si surfaces, the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag surface has been a focal subject in surface science. This is because the atomic structure of the surface had not been determined for more than two decades, in spite of its relatively small unit cell, $\sqrt{3} \times \sqrt{3}$, and great efforts devoted to this subject. Even the number of adsorbed Ag atoms per $\sqrt{3} \times \sqrt{3}$ unit cell and atomic species of the topmost layer had not been determined for a long time. In the early 1990’s, however, the controversies about the structure of the surface appeared to be settled finally. A model called the honeycomb-chained-triangle (HCT), which was first proposed on the basis of X-ray diffraction analysis [2], had been confirmed by various experimental and theoretical studies.

In achieving a consensus on the structure of the surface, two first-principles studies, reported by Ding et al. [3], and one of the present authors and co-workers [4], played important roles. Hereafter we refer to the former and latter studies as FPC-1 and FPC-2, respectively. In FPC-1, electronic structures and optimized structural parameters were calculated for several plausible models using the mixed-basis method within the local density functional (LDF) approach, and it was found that the HCT model has by far the lowest total energy. In FPC-2, electronic structure and scanning tunneling microscope (STM) images were calculated for the HCT model using the DV-Xao method within the LDF. It was shown that this model agrees very well with the observed STM images showing a honeycomb pattern of bright spots [5,6], although the model appeared to be inconsistent with the observed images at first sight. It is noted that the structural parameters used in FPC-2 were taken from...
Ref. [7], where the parameters were determined on the basis of experimental results from coaxial impact-collision ion scattering spectroscopy (CAICISS) and energy-minimization calculations using the Keating method.

Although both calculations support the HCT model and the overall features of the calculated electron density of states agree well, there is a distinct discrepancy between FPC-1 and FPC-2: the calculated electronic structure has an energy gap at the Fermi energy in FPC-2, but not in FPC-1. Very recently, Aizawa et al. obtained results that agree well with FPC-1 using the norm-conserving pseudo-potential method within the LDF [8]. Hereafter we call their calculations FPC-3. Since the method employed in FPC-3 is the most reliable and the structural parameters were not optimized from first-principles in FPC-2, it is reasonable now to rely on FPC-1 and FPC-3 rather than FPC-2. However, the origin of the discrepancy between FPC-2 and the others has not been clarified yet.

A more important finding in FPC-3 is that another model, which they call the inequivalent triangle (IET) one, was shown to be more stable that the HCT one by structural optimization without any symmetry constraints. This new model was supported by subsequent STM observations at low temperatures, where images show a hexagonal-lattice pattern of bright spots [8]. Now, another serious question arises: how should we interpret the observed experimental data at room temperature, which seem to be consistent with the HCT model? This question has not been answered yet.

Keeping the above situation in mind, we have reexamined the atomic and electronic structures of the surface using a first-principles method to (1) clarify the origin of the discrepancy between the previous calculations on the HCT model, (2) confirm the stability of the IET model using another method, and (3) examine the nature of the room temperature phase. In this paper, we describe the HCT and IET models and the method of the present first-principles calculations in Section 2. Then we present the calculated results on these two models in Section 3. Section 4 is devoted to calculations on other structural models, which have been performed to examine the nature of the room temperature phase. Finally, concluding remarks are given in Section 5.

2. The HCT and IET models and the method of calculation

Fig. 1 shows the HCT model improved by Katayama et al. [7] on the basis of experimental results from CAICISS and empirical calculations using the Keating method. In this model, three Ag atoms per $\sqrt{3} \times \sqrt{3}$ surface unit cell form the topmost layer. In a regular hexagon unit cell shown in Fig. 1(a) by solid lines, three Ag atoms form an equilateral triangle. These triangles are arranged in a hexagonal-lattice pattern. Below the Ag HCT layer, there is a Si layer, in which atoms form trimers. This Si trimer layer is followed by bulklike Si layers. As seen in Fig. 1(b), the second bulk-like layer is split into two layers. This splitting is caused by the fact that the Si–Si bond between the Si trimer layer and the first bulklike layer is tilted from the surface normal.

Fig. 2 shows the IET model. As can be seen from the figure, this model resembles the HCT one well, but notable differences are seen in the positions of the Ag atoms. These differences can be seen more clearly in Fig. 3, where the Ag atom positions in the IET model (open circles) are shown together with those in the HCT one (filled circles). First, a difference is seen in the “chained triangles”, equilateral triangles sharing apexes with their adjacent neighbors, indicated in Fig. 3 by solid and dashed lines for the IET and HCT models, respectively. All the chained triangles have the same size in the HCT model, while there are two sizes in the IET. Another notable difference is that the equilateral
triangle formed by three Ag atoms in a unit cell twists a little (by 6°) in the IET compared with that in the HCT. In the present calculation, the Si(111)-√3×√3-Ag surface based on the above models was represented by a slab model consisting of seven atomic layers, i.e. the topmost Ag layer, the subsequent Si trimer one followed by four bulklike Si layers (the second bulklike layer is split into two layers as mentioned previously), and a H layer. Here the H layer was introduced to terminate dangling bonds on the reverse surface. A periodic boundary condition was imposed, using the √3×√3 surface unit cell that corresponds to the regular hexagon shown in Figs. 1–3 and the unit length normal to the surface being 20.312 Å.

To calculate the electronic structures and the optimized structural parameters on the basis of the above model, the ultrasoft pseudopotential scheme proposed by Vanderbilt [9,10] was employed within the LDF. As for the exchange-correlation potential, the Ceperley–Alder form [11] parameterized by Perdew and Zunger [12] was used. The pseudopotentials were generated in the electron configurations of (1s)0.5, (3s)1.25(3p)1.75 and (4s)2.0 (4p)6.0(4d)10.0(5s)0.0(5p)0.0, with the cutoff radii for the local potential being 1.3, 2.1 and 2.5 bohr (1 bohr = 0.529 Å) for H, Si and Ag, respectively. For Ag, 4s, 4p and 4d components were also considered as the valence orbitals together with 5s and 5p, and the scalar-relativistic [13,14] ultrasoft pseudopotential was adopted with two reference energies for each angular-momentum component. The wavefunctions were expanded by plane wave-basis set with an energy cutoff of 16 Ry. For integration in k space, 12 and 18 special k points were used for the HCT and IET models, respectively. The total energy of the HCT models, however, was recalculated using 18 k-points when it is compared with the total energies of the other models. Both atomic and electronic degrees of freedom were optimized using the conjugate gradient method [15].

In optimizing atomic geometries, the reverse H and subsequent Si layers were fixed. The same structural parameters as those adopted in FPC-2 were used as the initial parameters in the optimization for the HCT model. In optimizing the IET model, the parameters optimized in the present calculation for the HCT were adopted as the initial one.

3. Calculated results on the HCT and IET models

Although there is little room for doubt about which we should rely on among FPC-1 to FPC-3, useful information must be provided to clarify the origin of the discrepancy.

Fig. 3. Comparison between the Ag atom positions in the HCT model (filled circles) and in the IET model (open circles). Thin solid lines and dashed lines indicate Ag chained triangles in the IET and HCT models, respectively. Thick solid lines denote the boundaries of unit cells.
This is the motivation for the present calculation for the HCT model.

In Table 1, we show the structural parameters of the HCT model determined in FPC-1, FPC-3, and the present calculation, together with those adopted in FPC-2, which were also adopted as the initial geometry of the present calculation. By comparing the initial and optimized parameters in our calculation, we can see a remarkable difference of 0.42 Å in the Si±Si distance (in the Si trimer layer) and in the splitting of the second bulklike Si layer. The difference in the Ag±Si bond length, 0.22 Å, is also fairly large, while it is at most 0.1 Å for the other parameters. As for the comparison among first-principles calculations, the agreement on the optimized parameters seems much better. Although a notable difference is seen in the distance between the Ag and the first bulklike Si layers (3.15, 3.01 and 2.86 Å for FPC-1, FPC-3 and the present one, respectively), the difference in the other parameters is less than 0.12 Å. In particular, the agreement between FPC-3 and the present one is very good.

Fig. 4 shows the calculated energy band structures for (a) the initial and (b) the optimized geometries of the HCT model. In Fig. 4(a) we can see a distinct energy gap of the order of 0.5 eV at the Fermi energy and a characteristic surface-state band with its minimum at the Γ point and increasing sharply along both Γ–K and Γ–M directions. Hereafter we refer to this surface-state band as S1. In addition, it can be seen that there are no empty bands besides S1 within 0.8 eV from the Fermi energy. These features, together with characteristics of the valence band, agree well with those seen in the calculated band structure of FPC-2. The only notable difference between FPC-2 and the present one is the energy position of the empty band other than S1: The bottom of these bands is nearly 2.0 eV above the Fermi energy in FPC-2. This discrepancy can be understood from the fact that linear-combination of atomic-orbital approaches like the DV-Xα method involve insufficient description of higher energy states because the number of basis functions is not enough.

As for the calculated energy band structure for the optimized geometry shown in Fig. 4(b), we can see that the energy gap seen in Fig. 4(a) disappears. This disappearance is caused by a downward shift of S1: the bottom of this band is located a little below the Fermi energy. Including this feature, the agreement between the present result and that of FPC-3 (Fig. 2(a) in Ref. [8]) is excellent. It may appear strange that the energy gap closes after geometry optimization, but this can be understood from the fact that S1 has the Ag–Si bonding character as Aizawa et al. pointed out [8].

From the above results, we can attribute the origin of the discrepancy seen in the energy band structures among previous calculations to the difference in structural parameters rather than the methods. In particular, the difference in the Ag–Si bond length is considered to be crucial, since S1 has the Ag–Si bonding character. In addition, we can also say that no serious discrepancy remains now among first-principles studies on the HCT model of the surface.

Next, we present the results on the IET model. First, we confirmed that the IET model is more stable than the HCT one and no energy barrier exists between these two models. The evaluated energy difference between the two models, 0.136 eV per unit cell, agrees satisfactorily with that obtained in FPC-3, 0.10 eV. Second, as for the optimized

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Table 1

| Parameter      | Present calculation | FPC-1 | FPC-3 |
|----------------|---------------------|-------|-------|
|                | Initial             | Optimized |       |
| d(Ag)          | 4.95                | 4.87  | –     | 4.88  |
| d(Si)          | 2.05                | 2.47  | 2.51  | 2.55  |
| d(trimer)      | 3.38                | 3.40  | 3.45  | 3.44  |
| z(Ag)          | 2.96                | 2.86  | 3.15  | 3.01  |
| z(Si)          | 2.21                | 2.24  | 2.30  | 2.29  |
| z(split)       | 0.57                | 0.15  | 0.2   | –     |
| Bond 1 (Ag–Si)| 2.65                | 2.43  | 2.54  | 2.47  |
| Bond 2 (Si–Si)| 2.43                | 2.43  | 2.51  | –     |

Table 2

| Parameter      | Present calculation | FPC-3 |
|----------------|---------------------|-------|
| d(Ag)          | 4.85                | 4.88  |
| d(Si)          | 2.51                | 2.58  |
| d(trimer)      | 2.91, 3.91          | 3.00, 3.89 |
| z(Ag)          | 2.93                | 3.01  |
| z(Si)          | 2.24                | 2.29  |
| z(split)       | 0.16                | –     |
| Bond 1 (Ag–Si)| 2.49                | –     |
| Bond 2 (Si–Si)| 2.35                | –     |

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Fig. 4. Energy band structures calculated for (a) the initial and (b) the optimized geometries of the HCT model. Here energies are measured from the Fermi energy (Ef).
structural parameters presented in Table 2 together with those obtained in FPC-3, the difference between FPC-3 and the present one is at most 0.08 Å, and thus the agreement is excellent. Lastly, the calculated energy band structure is shown in Fig. 5(b), together with that of the HCT model (Fig. 5(a)). The notable features of the IET model, which are different from those of the HCT one, are a further downward shift of S1 and energy splitting of some of the degenerated states. The energy band of Fig. 5(b) agrees very well with that obtained in FPC-3 (Fig. 2(b) in Ref. [8]), including the above notable features. In consequence, the present results for the IET model provide further confirmation of this model.

4. Calculation on other models having distortion similar to the IET

Aizawa et al.’s (FPC-3) results and the present ones shown in the previous section raise a new question: how can we understand experimental results at room temperature, which appear to be consistent with the HCT model? A possible answer for this question is that the HCT configuration is stable at room temperature, although it must not be at zero temperature. Another possible answer is that the structure at room temperature is fluctuating between various configurations, such as the two phases of the IET configuration corresponding to clockwise and anticlockwise twists from the HCT one.

To examine the possibility of the structural fluctuation, the calculations presented in the previous sections are insufficient. First, structural models other than the HCT and IET should be considered. In particular, structures where part of the Ag atoms twist from the HCT positions must be important, because it is energetically unfavorable to move all the Ag atoms simultaneously in the same way. Second, the periodicity imposed in the calculations, $\sqrt{3} \times \sqrt{3}$, is too strict: it is quite likely that a cell has the IET arrangement while an adjacent cell has another at the same time.

Keeping the above difficulties in mind, we have also performed the first-principles calculations for the models shown in Fig. 6(a)–(f). Here, we consider only the same distortion of Ag atom positions as that from the HCT configuration to the IET one. We, however, allow three Ag atoms in a cell to move independently, and also allow two directions of the distortion corresponding to clockwise and anticlockwise twists. For example, in Model (A) (Fig. 6(a)), only a single Ag atom in a cell moves to the position in the IET configuration, while the other two Ag atoms stay at undistorted positions, that is, the HCT sites. It is noted that Model (E) (Fig. 6(e)) coincides with the IET model. In the calculations, we imposed the same periodic boundary condition as before. The positions of the Ag atoms were fixed in the lateral directions, but were allowed to relax in the direction normal to the surface. Positions of atoms in the subsequent Si layers were also optimized as before.

Table 3 shows the calculated total energies of Models (A)–(F) measured from that of the HCT model. We can see that the most stable model is still the IET one (Model (E)), as expected. Another important point seen in the table is that the total energies of Models (A), (B) and (D) are lower than that of the HCT by 45.6, 80.3 and 0.4 meV per unit cell, respectively. The total energies of the other models are higher than that of the HCT, but only by 18.2 and 35.7 meV for Models (C) and (F), respectively. These results, in particular the small energy difference among various models, suggest that the surface structure is fluctuating between various configurations at room temperature, rather than staying in the HCT arrangement.

To further confirm this, consideration of a much larger area is necessary as mentioned previously. Because it is practically impossible to do this using first-principles methods, we are now performing Monte Carlo simulations (MCS) on the basis of the above first-principles results. In the effective Hamiltonian employed in the MCS, only the interaction between Ag atoms and their four nearest neighbors is explicitly considered. Other interactions are implicitly taken into account through determination of
parameters in the Hamiltonian from the above first-principles results.

Preliminary results of the MCS support that the structure of the surface is fluctuating at room temperature. They also suggest that the STM images observed at room temperature can be understood from the time-average of fluctuation. It is worth mentioning that similar interpretation of observed images is suggested for non-contact atomic force microscope images for the same surface on the basis of theoretical simulations [16]. In addition to the above, the preliminary results also suggest the existence of order–disorder transition below room temperature, which leads us to a natural understanding of the difference between the observed STM image at low temperature (triangular-lattice pattern) and at room temperature (honeycomb pattern). Judging from these preliminary results, we expect that all the experimental data concerning this surface can be understood on the basis of the present MCS.

5. Concluding remarks

By using first-principles calculations within the local density functional approach, we have reexamined the atomic and electronic structures of the Si(111)–$3\sqrt{3} \times \sqrt{3}$-Ag surface, which had been a focal subject in surface science for more than 20 years and has attracted renewed attention recently. First, from calculations on the HCT model, which had been believed to describe the structure of the surface, we found that a discrepancy among previous first-principles calculations concerning the energy band structure can be attributed to the difference in the structural parameters adopted in the calculations. Second, we have confirmed that the recently proposed inequivalent triangle (IET) model, where the positions of the Ag atoms are distorted a little from the HCT ones, is energetically more stable than the HCT. Next, we have also performed first-principles calculations for several other models that have a distortion of Ag atom positions similar to the IET one. The results suggest that the structure of the surface at room temperature is not the HCT configuration, but is fluctuating between various configurations.

The results obtained in the present calculations do not only deepen our understanding of the structure of this surface, but also provide useful information, which help analyses of experimental data on the properties of the surface. For example, the surface electric conductivity of the surface, for which interesting experimental results has been obtained recently [17], must be affected by the fluctuating nature of the surface. To clarify such effects must be an interesting future problem.

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| Model | Energy  |
|-------|---------|
| (A)   | −45.6   |
| (B)   | −80.3   |
| (C)   | 18.2    |
| (D)   | −0.4    |
| (E)   | −136.1  |
| (F)   | 35.7    |