Theoretical calculations of the scanning-tunneling-microscopy images of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface

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The scanning-tunneling-microscopy (STM) images of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface have been calculated from first principles for a structural model of the surface recently proposed, or the modified honeycomb-chained-trimer model, which is consistent with reported photoemission and inverse-photoemission spectra. The results show excellent agreement with reported STM images. Each bright spot corresponding to a protrusion in the reported STM images represents neither Ag nor Si atoms but rather corresponds to the center of each surface Ag trimer.

In spite of vigorous investigations with almost all surface-sensitive experimental methods in the last decade, the structure of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface is still controversial. Many structural models for this surface have been proposed, i.e., simple honeycomb,[1-4] missing top later,[4-8] embedded honeycomb,[9-11] atop trimer,[12] substitutional trimer,[13-18] honeycomb-chained-trimer,[19-22] centered hexagon,[23] silicon-adatom-vacancy,[24] and silver-honeycomb-chained-trimer[25] models, but none of them has obtained universal approval. For example, according to the electronic structure calculations by Nagayoshi,[26] none of the selected plausible models can explain the semiconducting character of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface, which has been observed by photoemission,[27] inverse-photoemission,[28] and scanning tunneling microscopy (STM).[18]

Recently, Aono and co-workers[29] have proposed a structural model for this surface, or the modified honeycomb-chained-trimer (HCT) model, on the basis of experimental results from coaxial impact-collision ion scattering spectroscopy[30] (CAICISS) and energy-minimization calculations using the Keating method.[31] This model is consistent with almost all reported experimental results regarding atomic geometry, but it has not been examined yet if this model is consistent with those experimental results that are related to electronic properties.[18,27,28] In this paper, we report the electronic structure of this model calculated from first principles and show that the results agree well with reported photoemission[27] and inverse-photoemission[28] data. Our main concern in this work, however, is that the modified HCT model appears to be inconsistent with reported STM images[3,4,17,18] at first sight. We have therefore calculated the STM images of the model on the basis of the calculated electronic structure mentioned above. The results show excellent agreement with reported STM images.[3,4,17,18] An important point is that each bright spot corresponding to a protrusion in the reported STM images represents neither Ag nor Si atoms but rather corresponds to the center of each Ag trimer. This is a good example showing that it is dangerous to simply conclude the atomic arrangement of a surface from its STM images.

The modified HCT model of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface is as follows [see Fig. 1 (Ref. 29)]. The topmost layer is formed by Ag atoms with the HCT arrangement[19] in which the intratrimer Ag-Ag distance is 5.1 ± 0.2 Å. Below the Ag HCT layer by 0.75 ± 0.07 Å, there is a Si trimer layer (three Si atoms per $\sqrt{3}\times\sqrt{3}$ unit cell), and this Si trimer layer is followed by bulklike Si layers. Because the Si—Si bond between the Si trimer layer and the first bulklike Si layer is tilted from the surface normal, the second bulklike Si layer is split into honeycomb and $\sqrt{3}\times\sqrt{3}$ layers with a large interlayer distance of about 0.6 Å.

The electronic structure of this model has been calculated from first principles with the local-density-functional approach[32,33] using the self-consistent numerical-basis-set linear combination of atomic orbitals (LCAO) method.[34] Slater's $X\alpha$ potential[35] with $\alpha=0.7$ was used as the exchange-correlation potential. An isolated slab consisting of six atomic layers, i.e., the Ag HCT, Si trimer, and subsequent four bulklike Si layers (the second bulklike Si layer is split into two layers as mentioned above), was adopted in the calculation. The dangling bonds of the lowest Si layer were terminated with hydrogen, the Si-H distance being 1.48 Å, which is the same as the Si-H distance in SiH_4.

The calculated energy-band structure is shown in Fig. 2. As we see, there is a distinct energy gap of 0.54 eV

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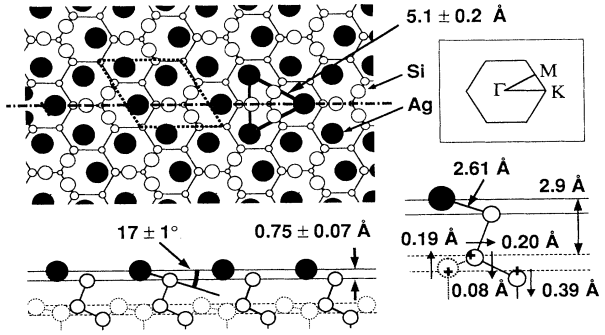

FIG. 1. Modified HCT model for the structure of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface. The Brillouin zone of the surface is shown as an inset.

around the Fermi level (E_F). This energy gap is not artificial owing to the finite thickness of the slab, since similar calculations for larger slab thicknesses resulted in essentially the same results. The existence of the energy gap agrees with photoemission,[27] inverse-photoemission,[28] and STM (Ref. 18) experiments. As far as we know, the modified HCT model is the only model that shows a distinct semiconducting character in electronic structure calculations. The number of valence electrons per surface unit cell in the model is even (three from three Ag atoms and nine from dangling bonds of three Si atoms) being consistent with the semiconducting character.

Figure 3(a) shows the calculated total density of states. Figure 3(b) shows the partial density of states contributed from the topmost Ag HCT layer and the next Si trimer layer, which is detected by surface-sensitive spectroscopic experiments. The density of occupied states in Fig. 3(b) agrees well with the photoemission spectrum reported by Yokotsuka *et al.*[27] in regard to the profile of the Ag 4*d* bands at about -5 eV below E_F and the structures between E_F and about -4 eV below E_F. The density of

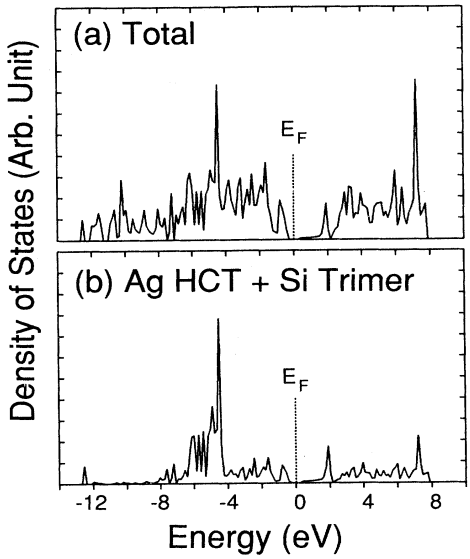

FIG. 3. Calculated (a) total density of states (DOS) and (b) partial DOS contributed from the top Ag HCT and the next Si trimer layers.

unoccupied states in Fig. 3(b) also agrees with the inverse-photoemission spectrum reported by Nicholls, Salvan, and Reihl[28] in regard to the structures between about $+1.5$ and $+5$ eV above E_F and a weak shoulder near E_F. The weak shoulder is observed only near the Γ point in the inverse-photoemission experiments, being consistent with the dispersion of the lowest unoccupied band in Fig. 2, which has a bottom at the Γ point.

STM images of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface have been reported by Demuth and co-workers[17,18] and by Wilson and Chiang.[3,4] As typically observed in an image taken at a tip bias of about -2 V, the STM images consist of bright spots corresponding to protrusions arranged in a honeycomb structure. At first sight, the STM images

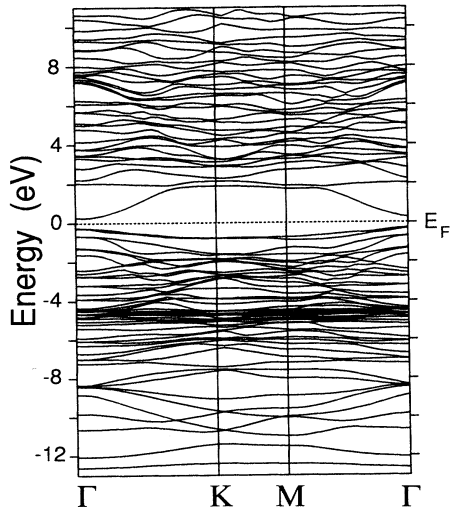

FIG. 2. Energy-band dispersions of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface calculated for the modified HCT model.

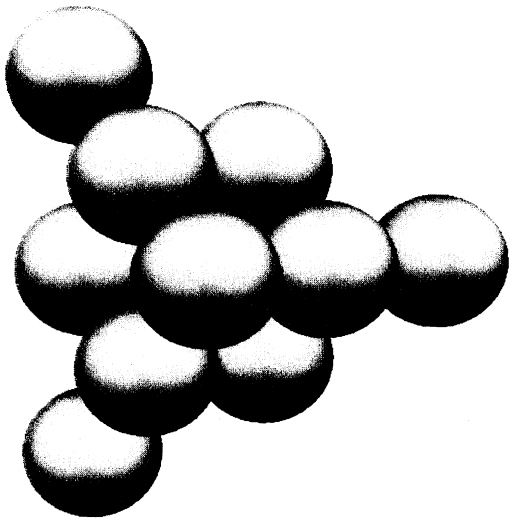

FIG. 4. The tip consisting of ten tungsten atoms with a [111] protrusion used in the STM image calculations.

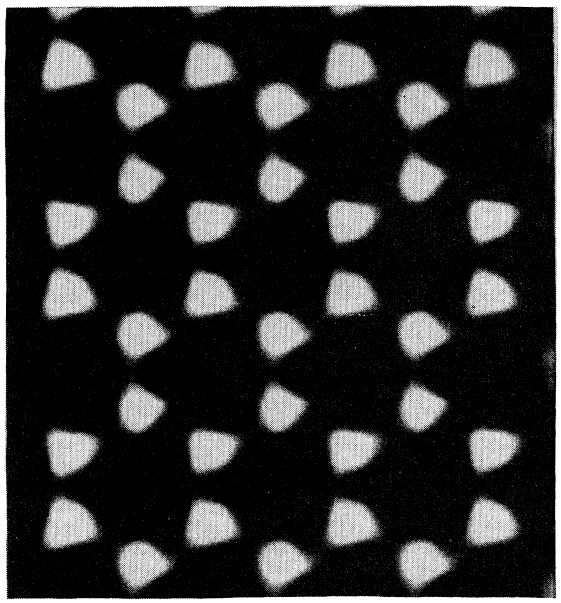

FIG. 5. Gray-scale image of the tunneling current in the logarithmic scale calculated for a bias voltage of −2.1 V applied to the tip. The distance between the Ag layer and the outermost W atom of the tip was 3.7 Å.

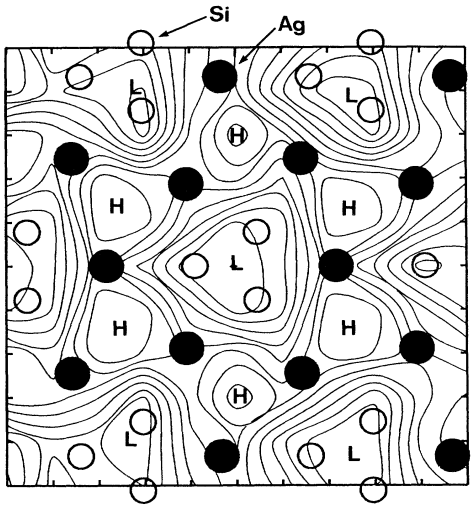

FIG. 6. Contour map of the tunneling current in the logarithmic scale calculated in the same condition as Fig. 4. Closed and open circles denote Ag and Si atoms, respectively. *H* and *L* indicate the maxima and minima of the tunneling current, respectively.

appear to be inconsistent with the modified HCT model because the Ag atoms in the topmost layer of the model have no honeycomb arrangement. We have therefore calculated the STM images of the model from first principles on the basis of the calculated electronic structure discussed above.

For this purpose, we adopted the formalism derived by Tsukada and Shima[36] for calculating the tunneling current. In their formalism, the electron wave functions of both a surface and a tip are expressed in a LCAO form, and the tunneling current is calculated with Bardeen's formula.[37] In the present calculations of the STM images of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface, the electron wave functions and energy dispersions of the surface calculated above have been used. Contributions from all the points in the Brillouin zone (see the inset of Fig. 1) have been correctly taken into account. As for the tip, a cluster consisting of ten W atoms with a [111] protrusion (Fig. 4) has been adopted, and its electron wave functions and energy levels have been calculated using the self-consistent numerical-basis-set LCAO method.

A typical current image calculated in this way is shown in Fig. 5 for a bias voltage of −2.1 V applied to the tip. Because of the existence of the energy gap around E_F, there is no current flow for bias voltages between −0.25 and 0 V. This is qualitatively consistent with experimental observation[18] in which no tunneling current was detected for bias voltages of −0.6 to +0.6 V. As seen in Fig. 5, a honeycomb structure of bright spots is observed. This image agrees well with the corresponding observed image.[3,4,17,18] The characteristic of the calculated image is preserved for bias voltages down to −3.0 V, which is also consistent with experimental observation.[3,18]

It is of importance to point out that the bright spots corresponding to protrusions in the observed STM image represent neither Ag nor Si atoms. As we see in Fig. 6, which shows the calculated contour map of the tunneling current, the center of each Ag trimer gives a bright spot. By examining the calculation in detail, it is found that unoccupied surface states, which mainly consist of the Ag 5*s* and 5*p* orbitals, are largely distributed in the center of the Ag trimer in the top view of the surface. This is the reason why the center of the Ag trimer gives a bright spot in the observed STM image. This is a good example showing that it is sometimes dangerous to simply conclude the atomic arrangement of a surface from its STM images.

To summarize, we have calculated the electronic structure and the STM images of the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface from first principles for the modified HCT model and shown that the results agree well with reported experimental results. In this way, it has been found that the modified HCT model is consistent not only with the experimental results regarding atomic geometry but with those related to the electronic structure.

We are grateful to Dr. M. Katayama and co-workers for their permission to use atomic coordinates in their modified HCT structural model before publication. We thank Dr. K. Kobayashi and Professor N. Isshiki for valuable discussions especially on computer programs for calculating the tunneling current. We also thank Professor N. Shima for helpful discussions regarding computer programs for DV-$X\alpha$ calculations. Numerical calculations were performed at the Computer Center of the University of Tokyo.

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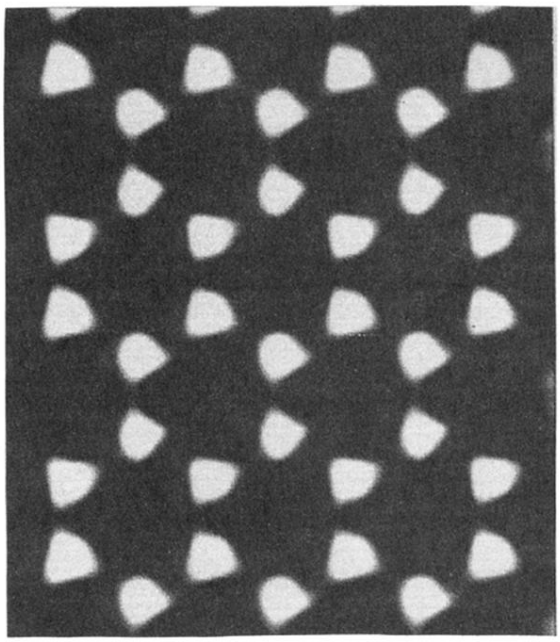

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