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Surface atomic structure of Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$

H. M. Zhang,* J. B. Gustafsson, and L. S. O. Johansson
Department of Physics, Karlstad University, S-651 88 Karlstad, Sweden
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Contrary to earlier reports, high-resolution scanning tunneling microscopy (STM) images of the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface show an inequivalent honeycomb structure at room temperature. The appearance of two different sizes in Ag trimers fits well with a recently reported inequivalent-triangle model instead of the widely accepted honeycomb-chain-trimer model. In addition, we found that Si trimers, which were "missing" in earlier STM observations, form a bright hexagonal pattern surrounded by a honeycomb chain from Ag trimers.

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Low temperature (LT) phase transition and surface symmetry breaking are currently under intensive studies for the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface.[1–4] This is partly based on a scanning tunneling microscopy (STM) observation.[3] At room temperature (RT), this surface shows a honeycomb pattern, while at LT it exhibits a hexagonal pattern. An inequivalent triangle (IET) model was suggested for the ground state,[2] instead of the honeycomb-chain-trimer (HCT) model that has been earlier proposed for this surface.[5–8] A theoretical simulation showed that the appearance of the RT HCT structure is a result of an average of the quick fluctuated LT IET structure.[4] The surface phase transition was supported by a surface x-ray diffraction and a photoemission study.[9,10]

As a prototypical system, Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ has been subjected to extensive STM investigations since the invention of this technique.[11–13] Both filled-state and empty-state STM images showed a honeycomb pattern, which was described by the HCT model.[5,6] Recent studies, owing to LT STM and powerful calculation as well, have provided a detailed picture of this surface. One observation is additional Ag atoms that are condensed into a solid phase at temperatures below 62 K.[14] When the extra Ag atoms are removed, the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface reveals its intrinsic electronic structure with well-resolved Si 2*p* core-level spectra and surface state bands.[15] An interesting finding is the hexagonal pattern shown by LT STM images, which is in contrast to the honeycomb pattern observed at RT.[2,11–13] A transition from a surface described by the symmetric HCT model at RT to an asymmetric IET model was proposed to occur at LT.[2–4] The transition temperature is believed to be somewhat below 150 K based on x-ray-diffraction and photoemission measurements.[9,10] The result is, however, in contrast with earlier photoemission reports that the valence-band spectra are essentially the same down to 70 K.[15,16]

The STM study was performed in a VT STM system from Omicron NanoTechnology GmbH. The STM tips were made from a W wire. The Si(111) samples cut from a single crystal wafer (Sb doped, 0.01 Ω cm) were pre-oxidized by an etching method and cleaned *in situ* by stepwise direct current heating up to 930 °C. This procedure resulted in a well-ordered 7×7 surface. Evaporation of 1 monolayer (ML) of Ag followed by annealing at 530 °C for 2 min resulted in a sharp $\sqrt{3}\times\sqrt{3}$ low-energy electron-diffraction (LEED) pattern. The sample was then annealed at ~600 °C for 1 min to remove extra Ag.

The basic structure in Fig. 1(a) is six bright protrusions that form a honeycomb pattern of the $\sqrt{3}\times\sqrt{3}$ reconstruction. In the HCT model [Fig. 1(b)], one Si trimer is surrounded by six Ag trimers, which are equally located at the corners of the honeycomb hexagons in the STM image. Figure 1(c) was obtained with a smaller bias and tunneling current at the same area where the image in Fig. 1(a) was recorded. Looking closely, there are two types of protrusions in this image: one is bright and the other is slightly darker. The bright (or less bright) features form a hexagonal pattern and give rise to a characteristic IET structure introduced in LT STM studies.[2,3] As illustrated in Fig. 1(d), the IET model differs from the HCT model by a slight rotation and displacement of the topmost Ag atoms. The result is that the small Ag trimer becomes brighter while the large Ag trimer becomes slightly darker in STM images. Obviously, the observed RT STM image in Fig. 1(c) fits well with the IET model.

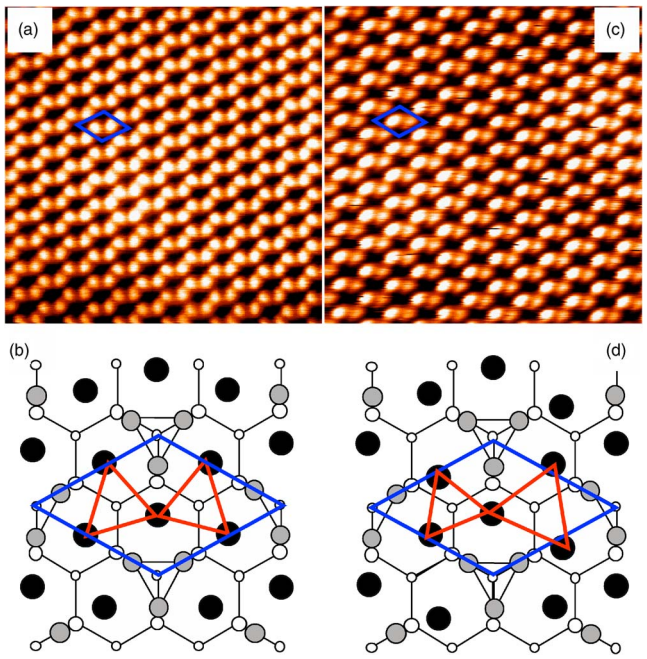

FIG. 1. (Color online) (a) STM image at RT, V_s=−0.6 V and I=1.0 nA, 84×84 Å. (b) HCT model. (c) STM image obtained at the same area as image (a), V_s=−0.3 V and I=0.3 nA, 84×84 Å. (d) IET model.

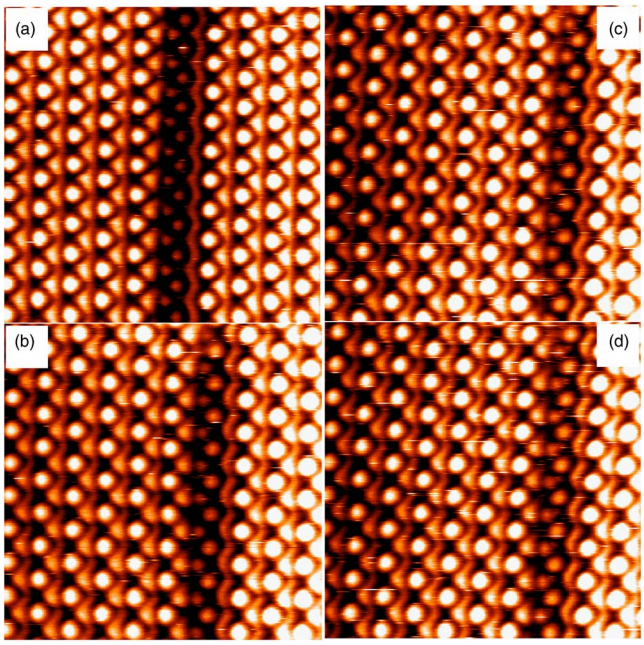

FIG. 2. (Color online) High-resolution STM image at RT, 64 $\times$64 Å. (a) V_s=−0.4 V and I=80 pA. (b) V_s=−0.1 V and I =50 pA. (c) V_s=0.1 V and I=50 pA. (d) V_s=0.05 V and I=50 pA.

To achieve high resolution of STM images, we have performed the measurements in various conditions. Figure 2(a) presents a well-resolved IET structure with a domain boundary that shifts the $\sqrt{3}\times\sqrt{3}$ reconstruction by half a unit cell. Both filled-state [Figs. 2(a) and 2(b)] and empty-state images [Figs. 2(c) and 2(d)] show two types of inequivalent triangle protrusions, which resemble the simulated STM pattern from the IET model.[2] These images once again demonstrate that the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface already shows the IET structure at RT.

The observation of an IET structure at RT is in sharp contrast to a HCT-IET phase transition reported in the literature, in which the IET structure was believed to be a LT phase.[2,3,9,10,17,18] To facilitate a comparison between RT and LT, we have also performed a LT STM study on the same surface. Two filled-state images in Fig. 3 were separately recorded at RT and 100 K with a sample bias of 0.3 V. Evidently, the two images present a quite similar IET structure. As illustrated in two line profiles, the main difference between RT and LT is the height contrast. Compared to the RT image, two types of Ag trimers at LT are well split with a large height difference of ~36 pm, while this value is only ~17 pm at RT. Except the height, we found that the surface atomic structures of Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ at RT and LT are essentially identical. This is clear evidence that no HCT-IET phase transition occurs between RT and LT.

We have investigated the surface electronic structure by using scanning tunneling spectroscopy (STS). Figure 4(a) shows a high quality STS spectrum from the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface at RT. Three surface state bands (S_1, S_2, and S_3) were found on this surface in the photoemission study.[7,19] The unoccupied surface bands previously have been studied by STS and inverse photoemission.[3,13,20] In Fig. 4(a), three structures are detected in the occupied surface-state region. The first peak, S_1, has a small surface density of states located at a sample bias of −0.1 V. The second feature appears as a shoulder located at −0.4 eV with respect to E_F (V=0). The spectrum has a strong peak that is located at −0.73 V below the Fermi level. Except an upward energy shift of 0.1 eV, the line shape of the occupied surface density of states in Fig. 4(a) is quite similar to the ones in Refs. 3 and 18 obtained at 62 and 6 K. Since the Fermi pinning position for this surface is just 0.1 eV above the valence-band maximum,[7] it implies that the unoccupied structures within 0–1 eV should originate from the surface states. In Fig. 4(a) there are more detailed features in the unoccupied state region than the earlier reports. The first empty-state peak (S_1^*) is located at 0.33 eV above E_F, which is consistent with the observations by the inverse photoemission and the other STS measurements. To be able to trace any change in surface electronic structure with temperatures, we have also performed LT STS measurements. Figure 4(b) shows an STS spectrum from the same surface at 100 K, which has lower quality than Fig. 4(a). Near the Fermi level the S_1 and S_1^* surface states are quite evident. Although the features appear weaker in the LT STS spectrum, we find that the LT spectrum has a line shape similar to the RT one. To conclude this part, there is no direct surface electronic evidence that supports the HCT-IET phase transition.

As shown in theoretical studies, the S_2 and S_3 surface states, which are degenerate at the $\bar{K}$ point in the HCT model, were predicted to split in the IET model.[2,17] Such a split was suggested in Ref. 3 based on two surface structures located at −0.4–−0.9 eV. However, a comparison between surface-state bands and STS spectra is not straightforward even though in some cases one may regard STS as angle-integrated photoemission. This is because one simple parabolic band with a certain band width may easily appear as two peaks near the band edges in a plot of density of states vs energy. The tip states are inevitably involved in the tunneling process as either the final or the initial state depending

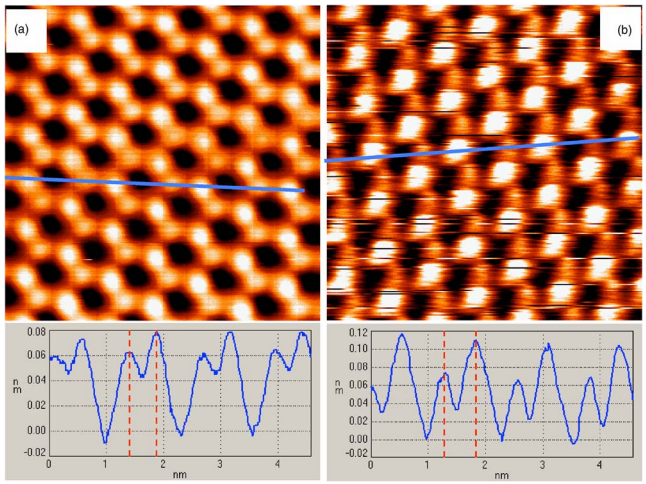

FIG. 3. (Color online) (a) STM image at RT, V_s=−0.3 V and I=0.01 nA, 46$\times$46 Å. A line profile indicates ~17 pm height difference between two neighboring protrusions. (b) STM image at LT, V_s=−0.3 V and I=0.1 nA, 46$\times$46 Å. A line profile indicates ~36 pm height difference between two neighboring protrusions.

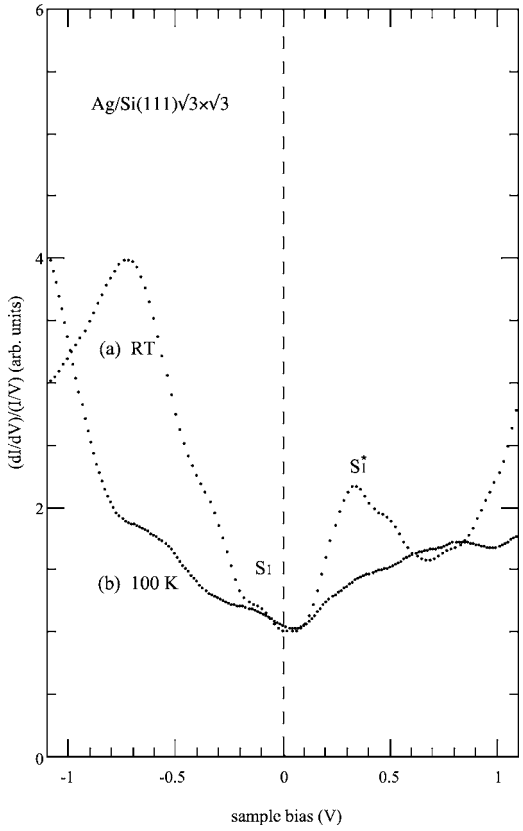

FIG. 4. STS spectra recorded from the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface. (a) RT and (b) 100 K. The spectra were spatially averaged.

on the current direction. The onset of surface conductance over a metastable tunneling barrier that varies on the tip-sample separation creates an uncertainty in energy positions. A fundamental problem of the STM and STS measurements is that they only sense the tails of wave functions at the surface protruding a few of Å into the vacuum. Surface electronic states that are localized between the first and second layer or very fast decay into vacuum are invisible in STM and STS. This is one main reason why Si trimers, which contain half of the surface units, have not been detected in earlier STM observations.

The Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface has been thoroughly studied by STM for decades.[3,11–13] Theoretical simulations concluded that the bright protrusion of the honeycomb pattern represents the center of the Ag trimer.[2,6,8] The Si trimer, on the other hand, was entirely mysterious since it appears as a black hole in the honeycomb pattern.[3,4,6,8,11–13] There is no big difference for Si atoms between the HCT and IET models, in which they are sitting slightly below the surface top plane. Unlike Ag trimers that conjugate each other, Si atoms form real isolated trimers in both the HCT and IET models. Initially each Si has three dangling electrons. Two of them bond to the neighboring Si atoms. The remaining one forms a big π bond, which also interacts with the surrounding Ag atoms. Even though STM could not visualize Si trimers, photoemission showed a strong surface component (S_1) in Si $2p$ core-level spectra.[15] Another technique that may "see" Si trimers is atomic force microscopy (AFM). Since AFM directly detects the force from individual atoms, it can be expected to sense the Si trimers even though they are sitting slightly below the top surface plan. However, the bright protrusions in AFM images were only interpreted as Ag trimers in a similar way as STM.[21,22]

Since the tunneling probability of STM depends on both the sample and the tip, the tip state may play an important role in the imaging process. In this study we show that the Si trimers can be directly observed under a special tip condition. Figure 5(a) was obtained at 100 K using a positive sample bias of 0.3 V and a tunneling current of 0.1 nA. The scan direction was moving from the bottom to the top in each image. Obviously, Fig. 5(a) was divided into three parts due to a tip reconstruction. At the bottom part the image shows the common honeycomb pattern. During the tip reconstruction, the tip state was not stable. This resulted in a mixed image in the middle part accompanying the bottom and the upper pattern. When the tip became stable again, the upper part presents another interesting pattern, i.e., large bright spots that form a hexagonal pattern are surrounded by six small dots that form a honeycomb pattern. The image in Fig. 5(b) was recorded just after image 5(a) was finished using the same conditions. The whole surface shows bright protrusions plus the honeycomb pattern. The image in Fig. 5(c) was taken just after image 5(b), but using a negative sample bias of −0.3 V. Compared to the empty-state image, the white spots in the filled-state image become even brighter and six small protrusions form a honeycomb network.

Compared to the atomic model, the large bright protrusions in Fig. 5 must be the "missing" Si trimers in the literature.[3,11–13] First, these protrusions form a hexagonal pattern in a way that the Si trimers should do. The second reason relies on the registry assignment of the Ag trimers as honeycombs in Fig. 5(a). The upper bright protrusions are positioned in the same line as the black holes of the honeycombs at the bottom part. The large bright spots thus are precisely sitting in the centers of the honeycombs. Since the assignment to the honeycombs from earlier STM and theoretical studies strongly points to Ag trimers, these bright

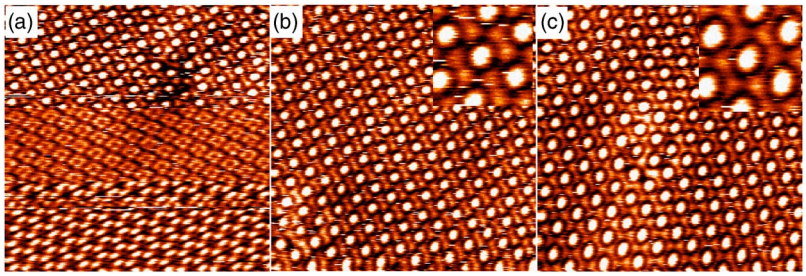

FIG. 5. (Color online) (a) STM image at 100 K, V_s=0.3 V and I=0.1 nA, 100×100 Å. (b) STM image obtained after image (a) with the same conditions. (c) STM image obtained after image (b), V_s=−0.3 V and I=0.1 nA.

spots find a natural explanation in terms of Si trimers. Here it is interesting to compare our STM images with AFM images. Figure 2 in Ref. 21 shows three AFM images with atomic resolution. Evidently, those images appear in a similar way as Fig. 5(b), i.e., one slight large spot surrounded by six protrusions. However, the authors in Ref. 21 assigned all the protrusions as individual Ag atoms. An alternative assignment would be one slight large spot as a Si trimer plus six protrusions from Ag trimers. Unfortunately, both the AFM study and the theoretical simulation fail to see the Si trimer as an alternative choice to explain the AFM image.[21,22]

The Si trimer that was observed after a tip reconstruction is a clear indication that a special tip state was involved in the tunneling process. Since the Si trimer shows up in both the filled-state and the empty-state STM image, this means a partially occupied surface state should be located at the Si trimer site. A most likely state would be the partially filled Si π bond. From a previous study of the origin of STM resolution, single atoms on the tip apex are required to obtain a lateral atomic resolution.[23] The W tip that was used in this study is very common in the literature. W on the tip apex has a dominant metallic d_z state (85%) at the Fermi level that can give a surface atomic resolution. However, the atom state that visualizes the Si trimer must be different from the one that only senses the Ag trimer. Since the Si trimer was entirely missing in earlier STM studies, this strongly indicates that W does not have a good tip state to "see" the Si trimer. In the tip-sample system there exist two other possibilities for single atoms on the tip apex, i.e., the Ag or Si atom. As a matter of fact, so far there are three kinds of major patterns that have been observed from the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface. They are honeycomb (HCT), inequivalent triangle (IET), and hexagonal spots plus honeycomb. After an initial formation of the $\sqrt{3}\times\sqrt{3}$ reconstruction, there always exist extra Ag atoms that are loosely bonded to the surface. At LT, these additional Ag atoms are condensed into the Ag trimer sites of the $\sqrt{3}\times\sqrt{3}$ surface.[14–16] One thus expects Ag atom can easily be picked up by the STM tip. But single Ag on the tip apex would more strongly interact with the Ag trimer and consequently senses the IET structure. On the other hand, single Si atom with a P_z state has a similar wave function as the Si π bond. This could result in an increased tunneling probability and thus to detect the Si trimers.

In conclusion, our high-resolution STM images clearly show an inequivalent triangle structure of the Ag trimers at room temperature. STM images at both RT and LT present a very similar IET structure. The STS result evidences a similarity between our RT spectrum and the LT one reported in earlier studies. It is clear that our STM data do not agree with the HCT-IET phase transition. In addition, we found that Si trimers form a bright hexagonal pattern surrounded by a honeycomb chain from the Ag trimers. Our finding indicates the important role of the tip state in the tunneling process and consequently the interpretation of STM images.

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*Electronic address: hanmin.zhang@kau.se

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