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Reexamination of the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface by scanning tunneling microscopy

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Scanning tunneling microscope images of the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface have a strong dependence on bias-voltage polarity. Empty-state images show a characteristic honeycomb pattern with two maxima per unit cell. Filled-state images show protrusions in the positions of Ag atoms in the honeycomb-chain-trimer (HCT) model. These images strongly support recent electronic-structure calculations that are based on the HCT model for this surface. The registration of the $\sqrt{3}\times\sqrt{3}$ features relative to the underlying Si(111) substrate is also measured. As part of this determination, the step height between adjacent $\sqrt{3}\times\sqrt{3}$ and 7×7 areas is discussed in terms of the electronic structure of the two phases as measured by scanning tunneling spectroscopy.

When approximately one monolayer (ML) of Ag is deposited onto a clean Si(111) surface and is then annealed to between 300 and 550 °C, the surface reconstructs into a structure showing a $\sqrt{3}\times\sqrt{3}$ unit cell. Beyond this simple fact, more details on this surface reconstruction remain elusive: The Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface has been studied by almost every surface analysis technique and yet its exact geometric structure remains controversial. Many different models have been proposed for this surface.[1,2] None of these models is currently universally accepted as being correct. Indeed, different experimental results have often supported completely different models. Previous scanning tunneling microscope (STM) results have contributed several pieces of information about this ordered phase. STM images show a honeycomb structure with two maxima per $\sqrt{3}\times\sqrt{3}$ unit cell,[3-6] and the registration of the center of these honeycombs with respect to adjacent areas of clean Si has been measured.[5,6] All of the more recent models of the $\sqrt{3}\times\sqrt{3}$ phase have accommodated both the appearance of the STM images and the accompanying registration information.

There have been a number of recent results that all agree on a structure that is referred to as the honeycomb-chain-trimer (HCT) model. Experimental support comes from x-ray diffraction,[7,8] reflection high-energy electron diffraction,[9] x-ray standing waves,[10] ion scattering,[11] and transmission electron diffraction.[12] Theoretical support comes from electronic structure calculations.[2,13] An important component of these theoretical calculations was to address an apparent discrepancy between the HCT model and images provided by scanning tunneling microscopy. At first glance, a honeycomb structure with two maxima per $\sqrt{3}\times\sqrt{3}$ unit cell would appear to be inconsistent with the arrangement of either the Si or the Ag atoms in the HCT structure. These calculations demonstrated that the spatial distribution of unoccupied states a few volts above the Fermi level (E_F) show a honeycomb arrangement of maxima that is consistent with the STM images, and that the maxima in the images are not associated with individual surface atoms.[2,13]

In this paper, we present results on the $\sqrt{3}\times\sqrt{3}$ surface from both STM and scanning tunneling spectroscopy (STS). Our data show that the topographic images have a strong dependence on voltage bias polarity. The empty-state images conform to the honeycomb appearance of previously published STM images, whereas the filled states correspond closely to the configuration of Ag atoms in the HCT model, in agreement with electronic structure calculations based on the HCT model. We also measure the registration of the $\sqrt{3}\times\sqrt{3}$ phase with respect to the underlying bulk Si lattice, and discuss the effects of the electronic structure on the apparent height difference between the $\sqrt{3}\times\sqrt{3}$ and the clean 7×7 structure, which has a bearing on the interpretation of the registration results.

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure of 8×10^{-11} torr. The chamber was equipped with a commercial STM,[14] a low-energy electron diffraction (LEED) optics, and facilities for sample preparation including cleaning, heating, and metal deposition. The Si(111) samples were 0.6 Ω cm *n*-doped wafers, cleaned *in situ* by thermal removal of the native oxide at 1150 °C, and characterized afterwards by both STM and LEED. The $\sqrt{3}\times\sqrt{3}$ surface can be produced by either Ag deposition on a hot substrate or thermal annealing after Ag deposition at room temperature (RT). In either case, the substrate was held at temperatures in the range of 350–550 °C, before cooling down to RT for STM imaging. The Ag deposition rate was typically about 0.05 ML/min, calibrated by a quartz-crystal thickness monitor, and Ag coverages were determined by timed exposure to the source.

Figure 1 shows a pair of images of the $\sqrt{3}\times\sqrt{3}$ structure taken over the same area of the sample. These images were taken in parallel, tunneling into the sample while rastering in one direction, and out of the sample while rastering in the other at a tunneling current of 1.29 nA. Panel (i) shows the empty states and panel (ii) shows the filled states at sample bias +1.6 V and −1.7 V, respectively. The registration between the two images was checked independently by comparing the positions of adatoms in an adjacent area of 7×7 in the same image which is not shown in this figure. The empty states show the

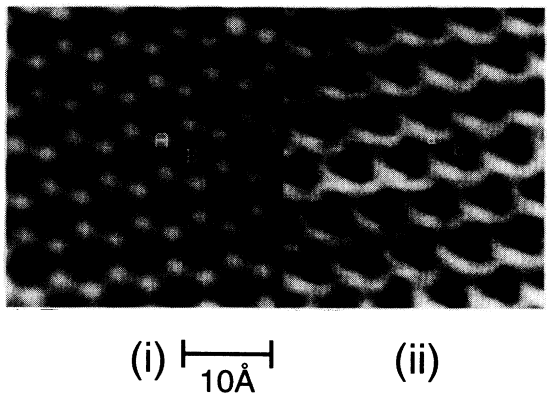

FIG. 1. A pair of images of the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ structure, showing (i) the empty states and (ii) the filled states. *A* and *a* mark the position of one of the empty-state maxima in both images. *B* and *b* mark corresponding minima in both images.

well-known honeycomb structure previously reported in the literature.[3-6] On the other hand, the filled states show a more complex structure, with each $\sqrt{3}\times\sqrt{3}$ unit cell having a deep triangular minimum surrounded by a pattern of maxima grouped in "trimers." The minima in both biases (marked as *B* and *b*) are over the same site. The arrangement of the empty- and filled-state maxima will be discussed below.

The HCT model of the $\sqrt{3}\times\sqrt{3}$ structure is shown in Fig. 2(a). This structure is derived from a bulk Si(111) termination by removing the top layer of Si atoms, forming trimers out of the remaining Si atoms, and then adding a full monolayer of Ag atoms in positions slightly distorted from a regular triangular lattice. The terminology honeycomb-chain-trimer refers to the arrangement of Ag atoms that was first proposed on the basis of x-ray diffraction.[7] The arrangement of the Si atoms and the relative positions of the Ag and Si atoms were determined by subsequent work.[2,10,11]

Electronic structure calculations and simulated STM images based on this model predict a honeycomb structure

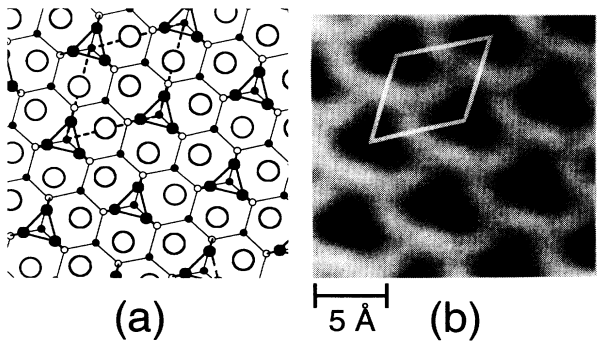

FIG. 2. (a) A diagram of the HCT model for the $\sqrt{3}\times\sqrt{3}$ surface, drawn to the same scale as (b) a filled-state image of this surface. The Si trimers in the HCT structure are shown as solid circles and heavy triangles. The Ag atoms are large open circles. One unit cell is outlined by a dashed line.

for empty states lying within 2 V of E_F which agrees with both Fig. 1 (i) and previously published images.[2-6,13] These calculations also predict that the filled states should show minima centered over the Si trimers, and maxima corresponding to the positions of the Ag atoms. Comparing the filled-state image [Fig. 1 (ii)] to the HCT model, we see that the filled states show minima with a distinct triangular shape surrounded by ridges between weak maxima that correspond to the positions of the Ag atoms. This can be seen most easily by sighting along lines in the $\langle 1\bar{1}0\rangle$ directions of the bulk surface and noting the zigzag character of the filled-state features which is due to the lateral shift of the Ag atoms away from a triangular lattice in the HCT model. This lateral shift groups the individual maxima into trimers. This is more apparent in the higher magnification image shown in Fig. 2(b). Figure 2(a) has been drawn to the same scale as this image. Comparison of the two images in Fig. 1 shows that the maxima in the empty states (*A*) lie in the center of each of the trimers (*a*) in the filled states. The Si trimers (in positions *B* and *b*) are not directly visible in either bias; they should correspond to a minimum in both images according to the theory. The close agreement of both the filled- and empty-state STM images with the calculations, and in particular the agreement with respect to the registration of the maxima in both voltage polarities, lend strong support to the validity of the calculations,[2,13] and hence to the HCT model for this surface.

It should be noted that the character of the filled-state images changes at low values of the bias. For $|V_s| > 0.8$ V, the images are as shown in Fig. 1(ii), whereas at biases within 0.75 V of V_s, the images show a honeycomb structure similar to the empty-state images. This same effect is seen in the filled-state images of van Loenen *et al.*[4]

Previous determinations of the registration between the features seen in the STM images and the underlying Si lattice have been made by examining the registry of the $\sqrt{3}\times\sqrt{3}$ maxima with respect to adatom positions in adjacent areas of the native Si(111)-7×7 structure.[5,6] Figure 3(a) is a diagram that corresponds to an image of a boundary between the two phases shown in Fig. 3(b). A triangular grid marks the positions of the unit-cell boundaries in the 7×7 structure. This grid is extended over the $\sqrt{3}\times\sqrt{3}$ area, and a comparison of the image and the diagram shows the registration of the Si trimers in the HCT model with respect to the Si bilayer underlying the Si 7×7 adatoms.

The interpretation given in Fig. 3 also relies on an assumption of a particular structure of the domain boundary with regard to the presence or the absence of a step at the boundary.[15] The two possible types of boundaries between the $\sqrt{3}\times\sqrt{3}$ domain and 7×7 domain are demonstrated in Fig. 4. If we choose the Si bilayer under the adatoms in the 7×7 structure as a reference, the $\sqrt{3}\times\sqrt{3}$ structure (Si trimers+Ag layer) can be built either one layer below or on top of the reference bilayer, each case producing the relative step height d_1 and d_2, respectively. While tunneling over such a phase boundary, the measured relative step heights varies with bias voltage. The two-step configurations can only be distinguished reliably by careful examination of the height difference across any

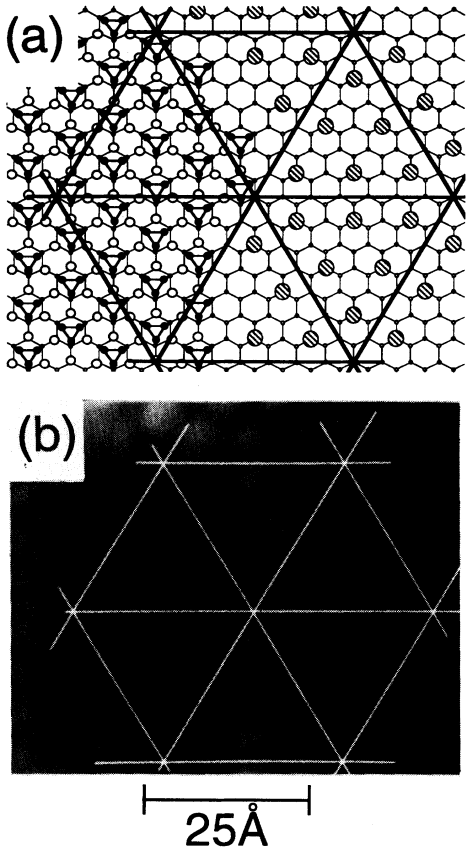

FIG. 3. (a) Schematic view of the HCT model for the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ alongside an adjacent area of 7×7 reconstruction. The HCT structure is drawn as in Fig. 2(a). Si 7×7 adatoms are hatched. The dimerization and stacking fault in the 7×7 structure are not shown for simplicity. A single height step along the phase boundary is not shown explicitly. (b) An empty-state image of a Si(111)-7×7/$\sqrt{3}\times\sqrt{3}$ domain boundary, taken at 1.6 V. Hexagonal grid lines in (a) and (b) correspond to each other.

given boundary at a variety of voltage biases. This is because the relative heights of the two phases can appear to be virtually the same at either type of step at different values of voltage bias.

At negative sample bias V_s (corresponding to tunneling from the filled states of the sample), the step height d_1 varied between 1.2 and 1.8 Å, and d_2 between 1.9 and 1.2 Å, with no clear trend versus the magnitude of V_s (V_s between -2.5 and -1.2 V). On the other hand, when tunneling into the empty states, there was a clear monotonic trend; d_1 increased from 1.2 to 3.1 Å and d_2 decreased from 1.5 to 0 Å as V_s moved away from E_F. To understand this behavior, we measured the electronic structure of the $\sqrt{3}\times\sqrt{3}$ and the 7×7 surfaces with scanning tunneling spectroscopy. Figure 5 shows STS data for both phases, taken during the acquisition of a single image to remove any differences due to tip electronic structure. The solid curve is associated with a 7×7 area and the dashed curve with an adjacent $\sqrt{3}\times\sqrt{3}$ area. The dI/dV curve for the 7×7 area is in general agreement with those published for clean Si(111)-7×7, showing states throughout the bulk band gap. On the other hand, the $\sqrt{3}\times\sqrt{3}$ spectrum shows semiconducting character with a surface-state gap of about 0.5 eV around E_F. This is in rough agreement with the calculations for the HCT model which predict a surface-state band gap (or pseudogap) of between 0.5 and 1 eV, with E_F near the bottom of the gap. This reduction in empty states above E_F for the $\sqrt{3}\times\sqrt{3}$ phase can explain the height difference between it and the 7×7 seen at different positive voltages. Over the same range of empty states ($V_s > 0$), the density of states from a 7×7 region would be higher than that from a $\sqrt{3}\times\sqrt{3}$ region. Thus a step of type d_1 would be enhanced, and a step of type d_2 would be depressed correspondingly. For the filled states, the ratio of the density of states for the $\sqrt{3}\times\sqrt{3}$ and 7×7 phases depends on the exact value of V_s. For the purposes of comparison, if the effects of electronic structure are totally ignored, then $d_1 \approx 1.2$ Å and $d_2 \approx 1.9$ Å. This assumes that the $\sqrt{3}\times\sqrt{3}$ Ag atoms and the 7×7 Si adatoms are 3 and 1.2 Å, respectively, above the underlying Si bilayer.[10,11,16]

Figures 3(a) and 3(b) correspond to the step type of height d_1. The 1×1 lattice drawn in Fig. 3(a) corresponds to the Si bilayer underneath the Si 7×7 adatoms

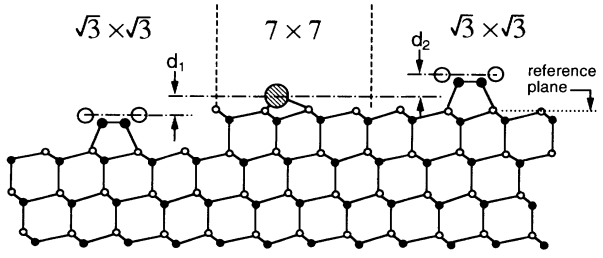

FIG. 4. Schematic view of the two types of boundaries between the 7×7 structure and the HCT model for the Ag/Si-$\sqrt{3}\times\sqrt{3}$ structure.

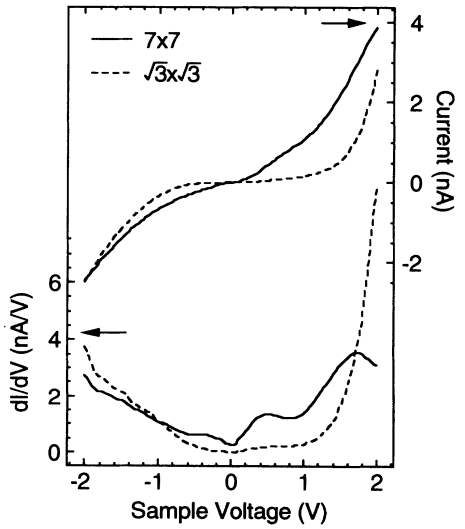

FIG. 5. STS spectra of the 7×7 (solid line) and the $\sqrt{3}\times\sqrt{3}$ (dashed line) surface structures.

which is actually situated *above* the $\sqrt{3}\times\sqrt{3}$ on the other side of the phase boundary. We have determined the registration between the $\sqrt{3}\times\sqrt{3}$ and 7×7 structures at both types of steps and have found two possible configurations. One is that shown in Fig. 3 which is consistent with the previous results of Wilson and Chiang.[5,6] In the context of the HCT model, this means that the Si trimers are found to lie over T_4 sites in the Si bilayer underlying the trimers, as illustrated in Fig. 2(a). The other has the Si trimers over H_3 sites in the Si bilayer. The details of when these different configurations arise on the sample surface will be discussed elsewhere.[17] However, we note here that the energy difference between the HCT structure in either configuration is very small.[18]

In summary, we have reexamined the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ surface using scanning tunneling microscopy. The structure seen in both filled and empty states, the registration between the filled- and empty-state maxima, the registration of the $\sqrt{3}\times\sqrt{3}$ unit cell with respect to adjacent areas of 7×7 structure, and the surface electronic structure measured by STS all support recent electronic structure calculations, which are in turn based on the honeycomb-chain-trimer model for this surface.

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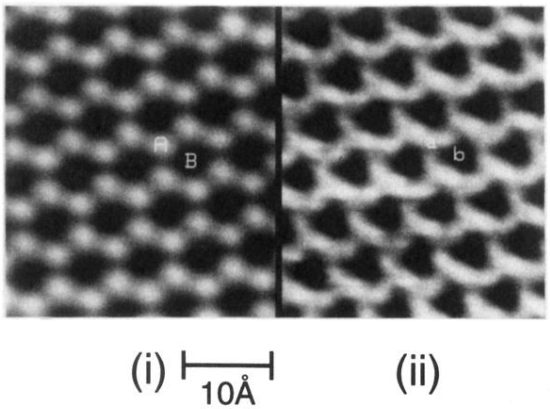

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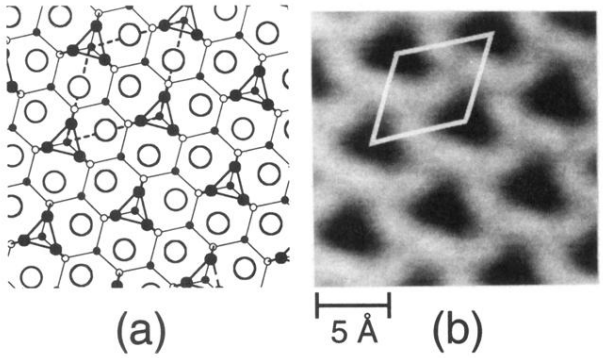

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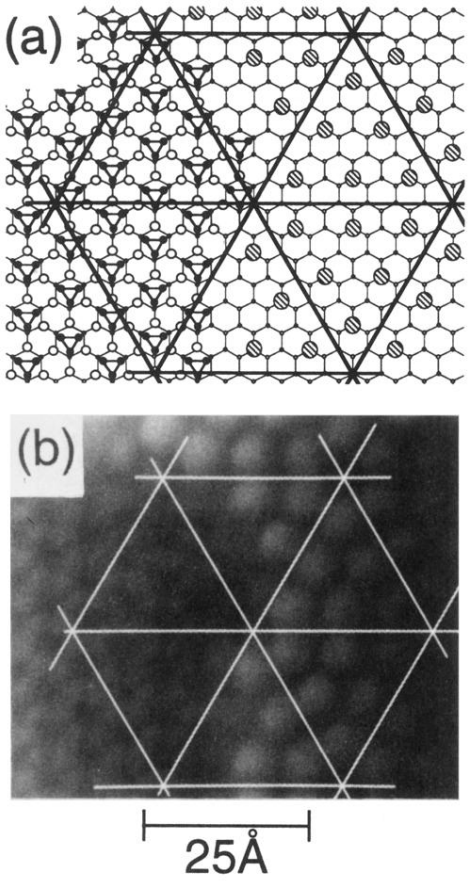

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