Brief Reports

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Evidence for trimer reconstruction of Si(111) $\sqrt{3}\times\sqrt{3}$-Sb: Scanning tunneling microscopy and first-principles theory

P. Mårtensson,* G. Meyer, N. M. Amer, E. Kaxiras,† and K. C. Pandey
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
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Scanning-tunneling-microscopy images of the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface show a trigonal lattice of protrusions, with a characteristic dependence on bias voltage. When probing filled surface states, the protrusions consist of three topographic maxima, while probing empty surface states gives a single maximum. These observations are interpreted in terms of an Sb-trimer model, the structure of which is obtained through first-principles calculations. Charge-density contours show that the three maxima seen when probing filled states can be directly related to the positions of the Sb-trimer atoms.

The adsorption of foreign atoms on semiconductor surfaces results in the reconstruction of the outermost surface layers. Concomitantly, the surface electronic properties are altered, a consequence which has significant fundamental and technological implications.[1] The adsorption of column-III and column-V metals on nonpolar semiconductors is of particular interest since these metals can fully passivate the surface dangling bonds, thus reducing its chemical reactivity. While column-III (Al,Ga,In) metals induce a $\sqrt{3}\times\sqrt{3}$ reconstruction on the Si(111) surface,[2-4] the column-V metal As has been shown to substitute the first-layer Si atoms, leading to a simple 1×1 structure with close to ideal positions of the surface atoms.[5] The occurrence of the Si(111)-(1×1)-As surface can be easily understood since it allows both the Si and As atoms to achieve their optimal bonding configuration: fourfold coordination for the Si atoms and threefold coordination for the As atoms. Since antimony atoms also prefer a threefold coordination, one might expect a similar 1×1 structure to occur upon deposition of Sb on the Si(111)-(7×7) surface. However, low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) studies[6] have shown that no well-ordered 1×1 structure can be obtained for Sb on Si(111). Instead, $\sqrt{3}\times\sqrt{3}$ and 2×2 reconstructions were obtained for an Sb coverage of one monolayer (1 ML).[7] In addition, more complicated reconstructions ($5\sqrt{3}\times5\sqrt{3}$ and $7\sqrt{3}\times7\sqrt{3}$) were obtained at ≈0.5 ML coverage. An x-ray photoelectron-diffraction study of the $\sqrt{3}\times\sqrt{3}$ reconstruction has indicated that this structure consists of Sb trimers in each $\sqrt{3}\times\sqrt{3}$ site.[8] However, the determination of structure by this method is both indirect and incomplete; e.g., the location and orientation of the trimers with respect to the substrate cannot be determined using this approach. Scanning tunneling microscopy (STM) is a direct tool for studying surface atomic and electronic structures. In the case of metals on semiconductors, a complication arises from the fact that STM does not provide direct chemical information. By combining voltage-dependent imaging with electronic-structure calculations, we show that the trimers reside *on top* of the Si substrate and that all the trimers have the same orientation. We have chosen the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface for this study because of the interesting questions relating to the bonding Sb atoms, which have a large covalent radius, and the Si(111) surface.

The experiments were performed in an ultrahigh-vacuum chamber, equipped with STM and LEED, at pressure of $\leq1\times10^{-10}$ mbar. Si(111)-(7×7) substrates were prepared by *in situ* thermal treatments of silicon samples with a doping of $\approx1\times10^{19}$ Sb atoms/cm^3. Large-area STM scans of the substrates displayed essentially perfect (7×7)-reconstructed domains larger than several thousand angstroms. Si(111)-Sb surfaces showing sharp LEED patterns were obtained by the evaporation of ≈3 ML of Sb with the substrate kept at 670°C, a temperature at which previous AES (Ref. 6) and x-ray photoemission (XPS) (Ref. 8) studies have shown that only 1 ML of Sb sticks to the surface. All STM images shown here were recorded in the constant-current mode, and no drift corrections were performed. We point out that all the features observed in the images presented in this paper have been reproduced in several different runs, using different tips, so that artifacts due to tip effects can be excluded.

Figure 1 shows a STM image of a 460×240 Å^2 region

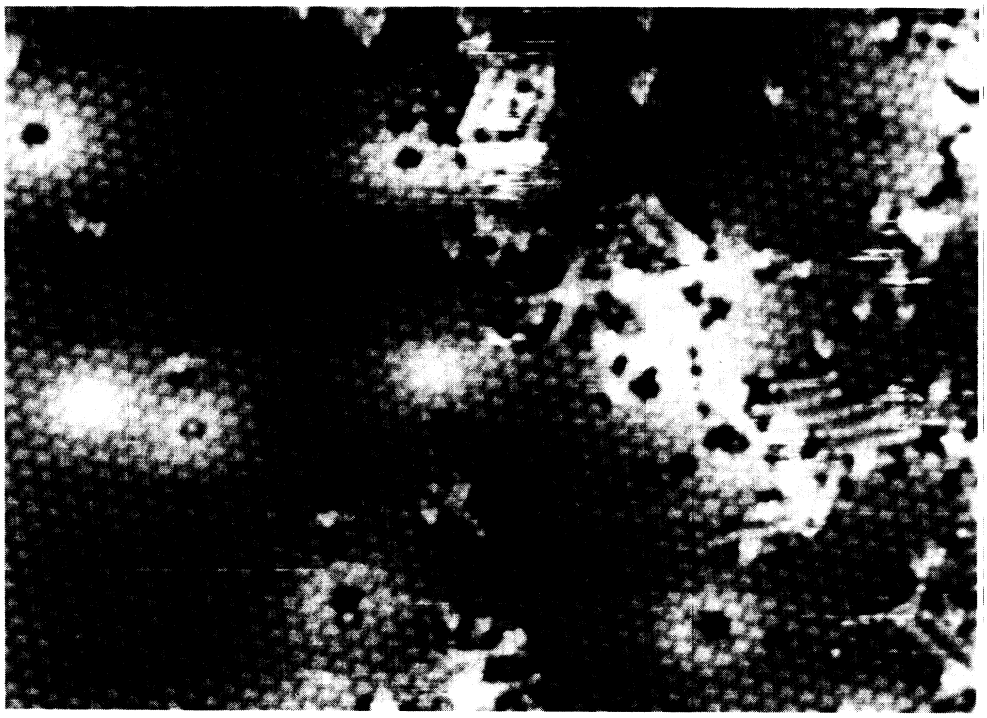

FIG. 1. 460×240 Å^2 STM image of Si(111) $\sqrt{3}\times\sqrt{3}$-Sb, acquired with a sample voltage of −2.0 V at a constant current of 0.1 nA. The topographic height is displayed by a gray scale ranging from 0 Å (black) to 6 Å (white).

of a Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface. This image, recorded at −2.0 V sample bias, is typical of images obtained by tunneling out of the filled surface states. Most of the surface is covered by a centered hexagonal array of threefold-symmetric protrusions. The separation between nearest-neighbor protrusions is a 6.5 Å along the [112] and [211] crystallographic directions, consistent with a $\sqrt{3}\times\sqrt{3}$ reconstruction rotated by 30° with respect to the ideal surface unit cell. A high-resolution image of the surface is shown in Fig. 2(a). Here, it is clear that the protrusions consist of three topographic maxima separated by approximately 3 Å. This strongly suggests the presence of trimers on top of the surface. This conclusion is supported by previous theoretical studies which predicted that column-V trimers form stable structures,[9] and by the photoelectron-diffraction data that implicate Sb trimers.[8]

One important feature that is evident from the images is that all the trimers have the same orientation with respect to the bulk:[10] lines connecting any two of the three topographic maxima forming the trimer run along the main surface crystallographic directions of type ⟨101⟩, which connect nearest-neighbor atoms in the ideal Si(111) surface. Also, the images of well-ordered regions show no evidence to suggest that parts of the surface have a subsurface stacking fault. Either there is no such stacking fault in the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface, or the entire surface has one, an issue that cannot be determined by STM or by the presently performed total-energy calculations. Additional experiments, especially normal incidence ion scattering, need to be performed to resolve this matter.

We have been able to obtain images for sample voltages in the ranges −2.5 to −1.5 V and from +1.0 to +2.5 V (with tunneling currents in the range 0.1–1.0 nA). In the region between −1.5 and +1.0 V, tunneling current versus voltage curves recorded over well-ordered $\sqrt{3}\times\sqrt{3}$-Sb areas show the presence of a band gap, in good agreement with the gap observed in combined photoemission and inverse photoemission experiments on this surface.[11] As mentioned above, all images recorded at negative sample voltages show the trimerlike protrusions. Images recorded at positive sample voltages, however, look quite different, with one single topographic maximum per $\sqrt{3}\times\sqrt{3}$ unit cell. This is illustrated in Figs. 2(b) and 2(c), which show STM images of the $\sqrt{3}\times\sqrt{3}$-Sb surface as acquired simultaneously[12] at sample voltages of +2.0 and −2.0 V, respectively. The crosshairs are in identical locations in both images. In the image acquired at −2.0 V, similar threefold-symmetric protrusions as in Figs. 1 and 2(a) can be seen. From the location of the crosshairs in Figs. 2(b) and 2(c), it is clear that the center of these trimerlike protrusions seen when tunneling out of the filled states of the surface coincides with the center of the protrusions seen when tunneling into the empty states. The images show no evidence for additional atoms around the trimers.

In order to understand the observed voltage dependence of the STM images, we have performed first-principles calculations in the framework of pseudopotential local-density-functional theory using a plane-wave

basis. The calculations were performed for a model in which Sb trimers reside on top of an unreconstructed, but fully relaxed outermost Si(111) double layer, as shown in Fig. 3. In this model, the Sb atoms are located almost vertically above the first-layer Si atoms with small lateral displacements toward the second-layer Si atoms. The Sb trimers thus formed are centered at the T_4 site. This position was chosen because it is the preferred site for adatoms (which also induce a $\sqrt{3}\times\sqrt{3}$ reconstruction) on the Si surface. The ideal Si(111) stacking sequence is assumed. Simple models with single adatoms over the T_4 or H_3 sites were not considered since they are inconsistent with the 1 ML Sb coverage as determined by AES (Ref. 6) and XPS.[8] Given this trimer model, a fully relaxed configuration for the atoms was obtained through minimization of the Hellmann-Feynman forces.[13]

The bonding of the Sb atoms to the Si substrate and to one another is exhibited in Fig. 3 by valence charge-density plots. It is clear that the tendency of Sb atoms to be threefold coordinated is taken into account in the model used, since each Sb atom has one bond to a Si atom below it and one bond to each of the two remaining Sb atoms in the trimer. Thus, three out of five valence electrons of each Sb atom participate in the formation of covalent bonds. The other two occupy lone-pair orbitals which protrude out of the surface. These orbitals are located 0.9 eV below the top of the valence band and give the dominant contribution to the lobes associated with the Sb atoms in the STM images [Fig. 4(b)].

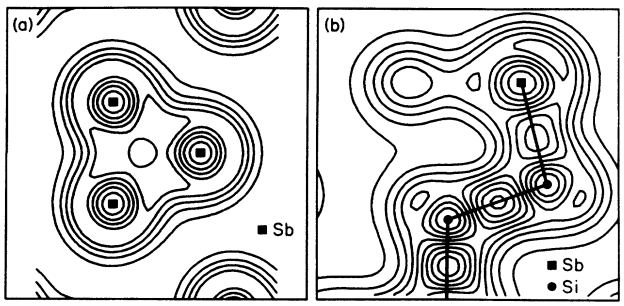

FIG. 3. Charge-density plots of (a) top and (b) side views of the Sb trimer model for the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface.

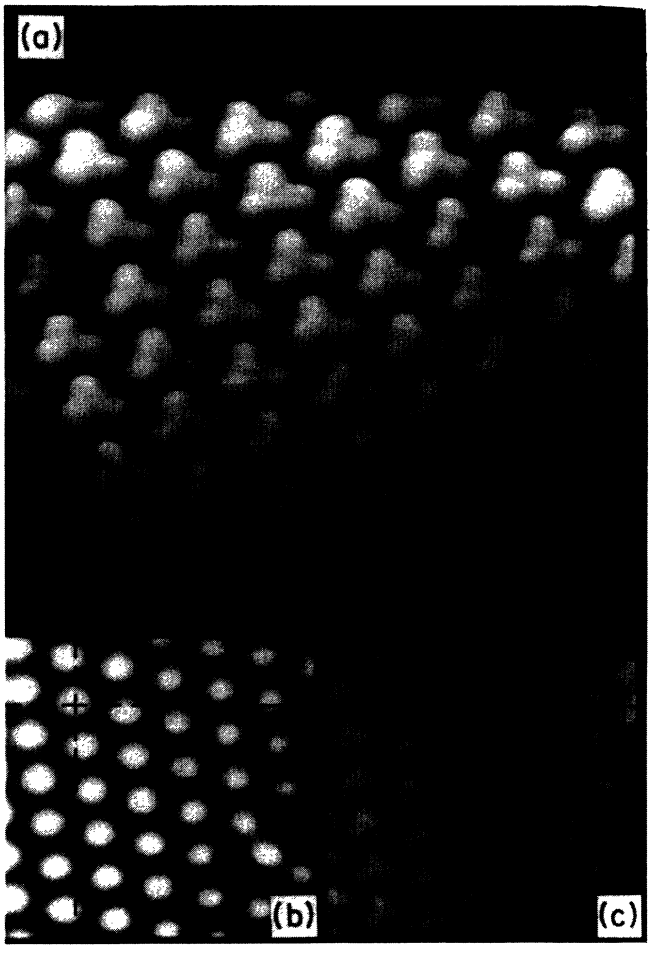

FIG. 2. (a) Perspective view of the $\sqrt{3}\times\sqrt{3}$-Sb surface, obtained at -2.0 V sample bias and a current of 0.1 nA. (b), (c) Constant-current images, acquired simultaneously with a sample voltage of (b) $+2.0$ V and (c) -2.0 V and a current of 0.1 nA. The crosshairs are located in identical positions in both images.

Now we explain the STM images through the electronic charge distribution corresponding to the optimal atomic configuration. To this end, we integrated the charge density of all bands within 2 eV above the Fermi level (E_F) and within 2 eV below E_F. This corresponds approximately to the experimental procedure of probing surface states at positive and negative samples bias of 2 V. A more-detailed comparison between theory and experiment should also take into account tunneling matrix elements between the surface and the probe; however, at present this is beyond any realistic treatment. The approximate comparison mentioned above proved sufficient to understand the basic features of the surface electronic structure.

The charge-density states up to 2 eV above E_F and those down to 2 eV below E_F are shown in Figs. 4(a) and 4(b), respectively. These contours were taken at a height of 2 Å above the position of the Sb ions, to enhance similarity to experiment, since STM probes the electronic

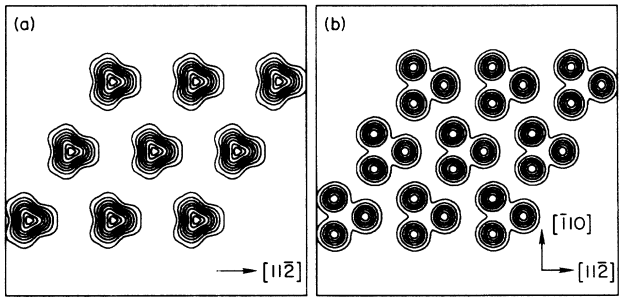

FIG. 4. Integrated charge-density contours corresponding to (a) empty states up to 2 eV above E_F, and (b) filled states down to 2 eV below E_F. This figure is a composite of nine $\sqrt{3}\times\sqrt{3}$ unit cells.

density at some (undeterminable) height above the atomic positions. The basic features of these contours do not vary much for a range of heights 0.5–2.0 Å above the positions of the Sb ions. We emphasize, however, that several reciprocal-space sampling points are needed, since the contours are sensitive to different points included. (For the contours displayed in Fig. 4, four different reciprocal-space points were used.) These contours possess a striking similarity to the STM topographs. The contours corresponding to filled states (below E_F) exhibit the three pronounced maxima that can be identified with the positions of the Sb atoms (they arise mainly from the Sb lone-pair orbitals mentioned earlier). The contours corresponding to empty states (above E_F) exhibit only one maximum at the center of the triangle formed by the Sb ions. This striking resemblance to the STM images for both filled and empty states leads us to suggest that the Sb trimer is indeed the reconstruction that occurs on the surface and no other structural features are needed to explain the STM images.

In summary, we have studied the Si(111) $\sqrt{3}\times\sqrt{3}$-Sb surface with STM and first-principles calculations. Excellent agreement between experiment and theory is obtained for a model with the Sb atoms residing nearly on top of the first-layer Si atoms, forming trimers centered at the T_4 sites. This unexpected finding is in sharp contrast with the previously studied case of As where, despite the chemical similarity between As and Sb, As substitutes the first-layer Si atoms resulting in a 1×1 structure. This could be due to a number of reasons, such as the difference in the covalent radii of As and Sb, as well as different sticking coefficients, diffusion rates, and other kinetic factors. Further studies are needed to clarify this matter.

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*Present address: Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden.

†Present address: Complex Systems Theory Branch, Condensed Matter and Radiation Science Division, Naval Research Laboratory, Washington, D.C. 20375-5000.

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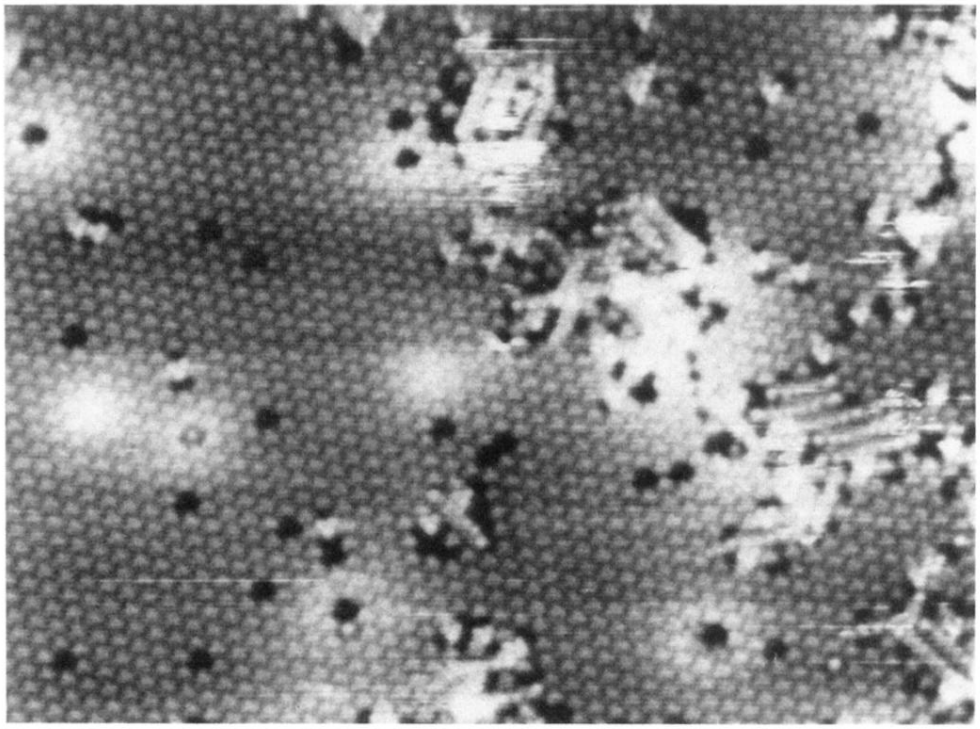

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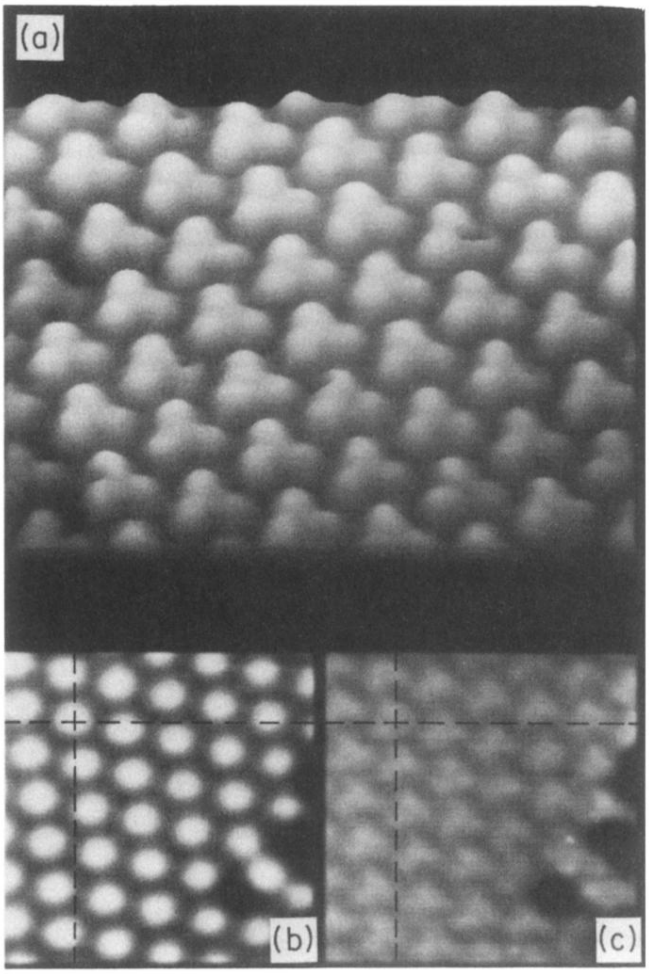

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