

Sb/Si(110) 2×3 surface studied with scanning tunneling microscopy: Evidence for adatom reconstruction

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Scanning tunneling microscopy (STM) has been used to study the Sb/Si(110) 2×3 surface at room temperature. The STM filled-state image shows the presence of four protrusions per unit cell while the empty-state one presents two broader protrusions. These results are consistent with single Sb adatoms saturating three Si dangling bonds. [S0163-1829(99)03840-0]

The interaction of Sb atoms with silicon surfaces has been the subject of much research in recent years because antimony is the most commonly used donor dopant in Si-MBE (molecular beam epitaxy). Apart from the most studied Si(100) and Si(111) surfaces,¹⁻³ there has recently been some interest in the study of the interaction of Sb atoms with the Si(110) face.⁴⁻⁷ This is mainly due to strong experimental difficulties of the Si(110) surface preparation. In fact, Ichinokawa *et al.*⁸ showed that only one superstructure exists on the clean Si(110) face, namely a 16×2 reconstruction, and that all other different reconstructions reported in the literature⁹ are Ni-stabilized.

The adsorption of Sb on the Si(110) face forms a 2×3 reconstruction whose electronic properties have been studied with angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and surface differential reflectivity (SDR).⁶ ARUPS showed the existence of three induced Sb states in the silicon valence band while in the SDR spectrum a semiconducting behavior with an optical gap larger than 3.5 eV has been observed.

A core-level spectroscopy^{10,11} study of the clean Si(110) 16×2 reconstruction showed that the Si $2p$ spectra display strong similarities with those of the Si(111) 7×7 reconstruction,¹² pointing to the presence on the 16×2 reconstruction of building blocks (adatoms, rest atoms, pedestal, and dimer atoms) similar to the 7×7 one. Core-level spectroscopy was also used to study the Sb/Si(110) 2×3 (Ref. 7) surface showing the presence of a strong interfacial component (S) shifted 0.24 eV on the high-binding-energy side with respect to the bulk peak. Such a shift has been explained as mainly due to charge transfer caused by the electronegativity difference between Sb and Si atoms.

In this paper we present a scanning tunneling microscopy (STM) study of the Sb/Si(110) 2×3 surface at room temperature. The STM filled-state image shows the presence of four protrusions per unit cell while the empty-state one presents two broader protrusions. These results are consistent with single Sb adatoms saturating the Si dangling bonds.

The experiments were performed in an ultrahigh-vacuum system (base pressure $<1\times 10^{-10}$ mbar) described elsewhere.¹³ Monocrystalline n -type silicon samples with the bulk doping level of $10^{14}/\text{cm}^{-3}$ have been used. The surface crystallographic orientation corresponded nominally to the (110) plane within a 1° deviation. The samples were mechanically polished and etched according to the procedure by Ishizaka and Shiraki.¹⁴ They were thoroughly outgassed at 500 °C in ultrahigh vacuum and the final cleaning was performed by heatings with direct current (1000–1200 °C, 10 min, slow cooling) in a vacuum of less than 3×10^{-9} Torr. A quite distinct 16×2 low-energy electron-diffraction (LEED) pattern with low background was observed.

Sb was evaporated from a thoroughly outgassed Knudsen cell at a rate equivalent to 0.5 ML/min, as monitored with a quartz microbalance. 1 ML of Sb is defined as the site density for the unreconstructed surface which is 9.6×10^{14} atoms/cm². Pressures during Sb deposition and sample heating did not exceed 1.0×10^{-9} Torr. Around 2 ML of Sb have been evaporated onto a clean 16×2 surface held at room temperature and by further annealing at about 650 °C in order to get rid of Sb atoms exceeding one monolayer. This produced a surface with a sharp 2×3 LEED pattern with very low background. All temperatures were measured with an infrared pyrometer.

It is hard to establish the actual Sb coverage on the surface due to the fact that the sample was annealed at 650 °C after Sb evaporation and some Sb atoms could have been desorbed giving a different Sb thickness than measured by the quartz microbalance. According to Zotov *et al.*,¹⁵ two different Sb-induced 2×3 reconstructions are possible on this surface: one that corresponds to a Sb coverage of $\frac{1}{3}$ of a monolayer and the other to 1 ML. All STM images shown here were recorded in the constant-current mode, and no drift corrections were performed. STM images have been recorded for several 2×3 -Sb surfaces, obtained for somewhat different initial amounts of Sb, and the results show that the STM images of this surface are quite reproducible.

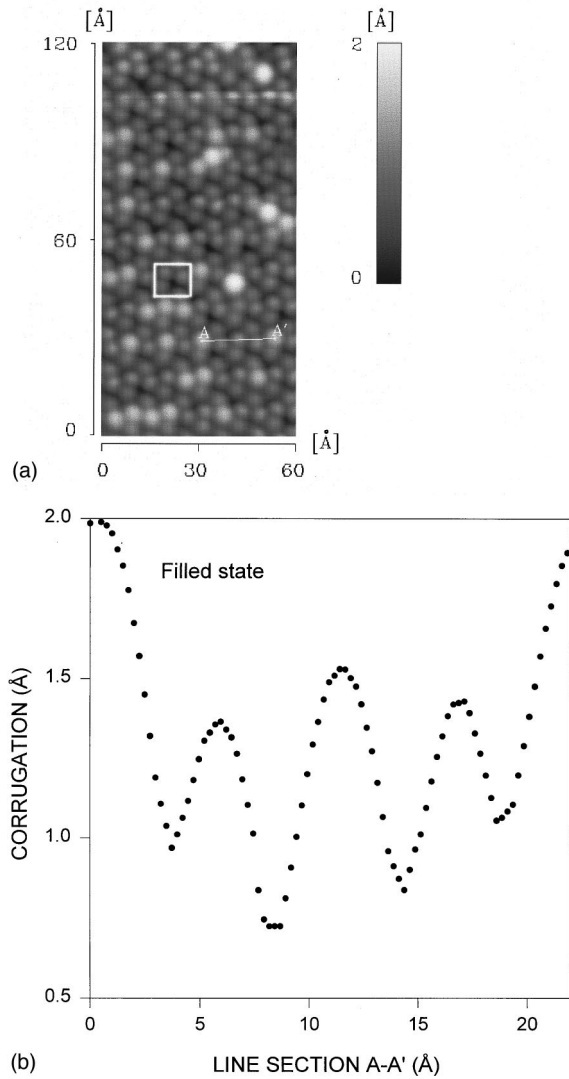


FIG. 1. (a) Filled-state STM image ($10 \times 10 \text{ nm}^2$) of a Sb/Si(110) 2×3 surface. -2.4 V sample bias, 1.5 nA tunneling current. (b) Surface height along the cross section A-A' of (a). The zero level on the y axis is arbitrary.

Figure 1(a) shows a STM image of a $60 \times 120 \text{ \AA}^2$ region of a Sb/Si(110) 2×2 surface. This image, recorded at -2.4 V sample bias, is typical of images obtained by tunneling out of the filled surface states. Within each 2×3 surface unit cell (the white square of size, approximately $10 \times 11 \text{ \AA}^2$) four equivalent protrusions are visible. Most of the surface is covered by such structures and the separation between nearest-neighbor protrusions is around 5.5 \AA . Figure 1(b) shows the surface height along the cross section A-A': the perfectly spherical shape of the protrusions strongly suggests the presence of single Sb adatoms on top of the surface, so that it may be possible that the 2×3 -Sb reconstruction that we observe is due to four Sb adatoms saturating the twelve Si dangling bonds present on the 2×3 unit cell. The four protrusions observed in the STM filled-state images are also consistent with the trimer model of Zotov *et al.*,¹⁵ who suggested the formation of four trimers of Sb atoms per unit cell on top of the last layer of Si atoms. In this case, one would expect some kind of triangular shape for the protrusions ob-

served by STM, as in the case of the Sb/Si(111) $\sqrt{3} \times \sqrt{3}$ (Ref. 16) surface where Sb trimers are formed on top of the Si(111) 7×7 reconstruction. However, we have to take into account the possibility that our STM tip might not be able to resolve the individual atoms in a trimer.

We have been able to obtain images for sample voltages in the ranges from -3.0 to -1.0 V and from $+1.0$ to 3.0 V (with tunneling currents in the range 0.1 – 3.0 nA). In the region between -1.0 and 1 V , tunneling current versus voltage curves recorded over well-ordered 2×3 areas show the presence of a band gap, in good agreement with the gap observed in photoemission experiments.⁶

By looking at the STM image represented in Fig. 1(a), it is possible to see that one protrusion is quite often brighter than the other three. This should indicate either the presence of one extra silicon atom directly positioned at the surface under the Sb adatom, or it may be due to some kind of defects at the Sb-Si interface: the presence of defects such as misfit dislocations and vacancies might be needed to accommodate the 16% difference in covalent radii between Sb and

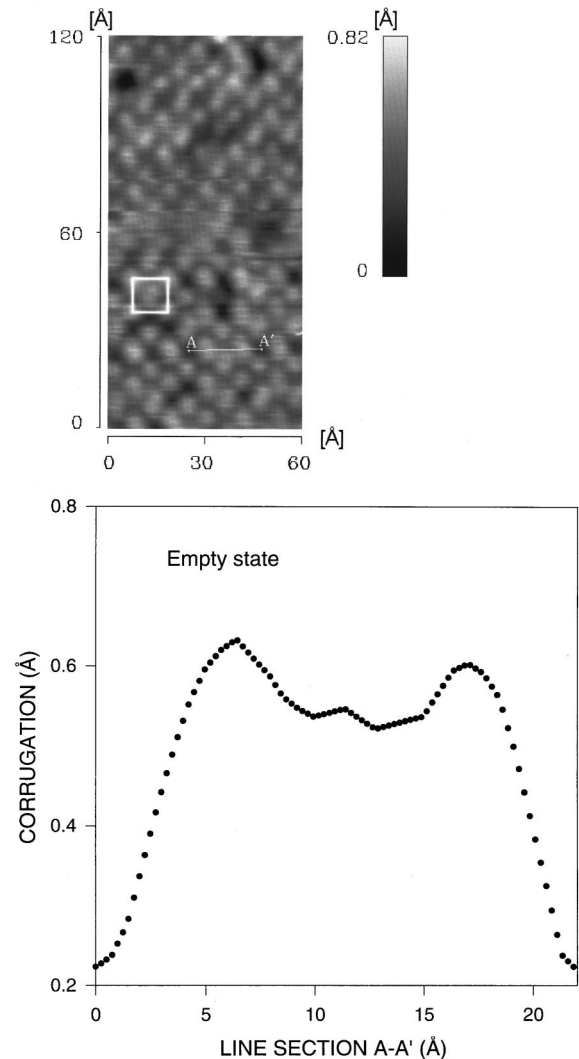


FIG. 2. (a) Empty-state STM image ($6 \times 12 \text{ nm}^2$) of a Sb/Si(110) 2×3 surface. $+2.0 \text{ V}$ sample bias, 1.5 nA tunneling current. (b) Surface height along the cross section A-A' of (a). The zero level on the y axis is arbitrary.

Si. It is worthwhile to observe that core-level photoemission data⁷ of the Sb 4*d* show a single well-resolved doublet, consistent with Sb as adsorbed in a unique position without any multisite adsorption. In this respect, additional experiments, especially x-ray diffraction, need to be performed to resolve this matter.

Images recorded at positive sample voltages look quite different with two single topographic maxima per 2×3 unit cell. This is illustrated in Fig. 2(a), which shows an empty-state STM image ($60 \times 120 \text{ \AA}^2$) recorded at a sample voltage of +2.0 V and taken in the same region of Fig. 1(a). The white square represents the same unit cell as in Fig. 1(a): one maximum is located at the center of the cell, i.e., between the four protrusions observed in Fig. 1(a), while the other is shared at the four corners. Figure 2(b) shows the surface height along the cross section $A-A'$, corresponding to the same line of Fig. 1(a). In the case of Fig. 1(b), we can clearly see a maximum at the two edges of the line and three relative maxima in between; in Fig. 2(b), we have two minima at the edges of the line and a broad structure around the three central peaks of Fig. 1(b). This gives the indication that while the filled-states STM image represents the position of Sb adatoms, i.e., Sb atoms are negatively charged, the empty-state STM image might represent the Si atoms participating in the bonds with the Sb adatoms: such Si atoms suffer charge deficiencies due to the lower electronegativity as compared with Sb.

A possible geometrical arrangement of the Sb/Si(110) 2×3 reconstruction, in agreement with the filled- and empty-state STM images, is shown in Fig. 3. It is clear that the tendency of Sb atoms to be threefold coordinated is taken into account in the model proposed since each Sb adatom is in a hollow position and bonds to three Si surface dangling bonds. 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 should give the dominant contribution to the four protrusions, observed in the filled-state STM images, that can be identified with the positions of the Sb at-

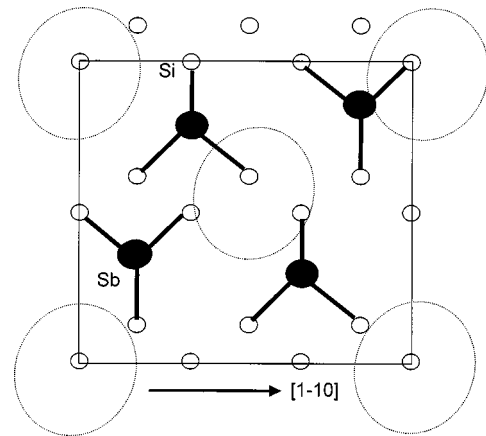


FIG. 3. A schematic rendition of the filled- and empty-state STM images showing the locations of the different contributions inside a 2×3 unit cell. The surface layer consists of Sb atoms (filled circle) while the Si atoms (empty circle) are located in the layer below. The dashed circles represent the broad maxima observed in the empty-state STM images.

oms. Four Sb atoms can saturate twelve Si dangling bonds of the clean Si(110) 16×2 surface, giving rise to a Sb-induced 2×3 reconstruction. The Sb geometrical arrangement in the model of Fig. 3 corresponds to a Sb coverage of $\frac{1}{3}$ of a monolayer. The dashed circles at the center and at the four corners of the SBZ represent the empty-state STM images, mainly localized over the Si atoms participating in the bonds with the Sb atoms.

Finally, we want to 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.

In summary, we have studied the Sb/Si(110) 2×3 surface with voltage-dependent STM. The filled-state images are consistent with an Sb adatom in a hollow position and saturating three Si surface dangling bonds. The formation of Sb trimers at the surface is unlikely to happen.

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