

Adsorbed and substituted Sb dimers on GaAs(001)

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The surface reconstructions formed on Sb-terminated GaAs(001) have been investigated using scanning tunneling microscopy (STM). Following Sb deposition on the (2×4) reconstructed GaAs(001) surface, (1×4) , (1×3) , and (2×4) phases are observed in order of increasing annealing temperature. Structural models for these phases are discussed based on an examination of the STM images and previously published core-level photoemission data. Considerable differences exist between the unit cell structure and ordering on the clean GaAs(001) and Sb-induced (2×4) surfaces. Following desorption of Sb at 580°C , a (4×2) structure is observed that appears to be identical to the reconstruction produced by annealing the clean GaAs(001) surface at this temperature. This result shows that a previously proposed model for the clean GaAs(001)- (4×2) phase is incorrect. [S0163-1829(96)52624-X]

The interaction of Sb with the GaAs(001) surface has recently been the subject of a number of experimental investigations. Interest in this material system stems in part from a need to understand the bonding and atomic configuration during the epitaxial growth of GaSb/InAs (Ref. 1) and GaSb/GaAs (Ref. 2) layers. Synthesis of Sb/GaAs heterojunctions and multilayers has also attracted attention as model systems for semimetal-semiconductor heteroepitaxial growth.³ While the gross morphology of GaSb/GaAs layers has been investigated with atomic force microscopy,² Maeda, Watanabe, and Oshima⁴ have used both reflection high-energy electron diffraction (RHEED) and core-level photoelectron spectroscopy (PES) to study the reconstructions formed at the Sb-terminated GaAs(001) surface. The Sb-induced GaAs(001)- (2×4) structure has also been investigated using the x-ray standing-wave (XSW) technique, where the bond lengths of Sb dimers present at the surface were evaluated.⁵ Despite the importance and interest in this material system, there are no accepted structural models for the surface reconstructions formed on Sb/GaAs(001).

In this paper we present a scanning tunneling microscopy (STM) study of the Sb-terminated GaAs(001) surface. An examination of STM images of the various surface reconstructions, whose periodicity was previously determined solely by RHEED,⁴ enables us to propose atomic structural models for these phases. We discuss notable differences in the structure and ordering of the Sb- and As-terminated GaAs(001)- (2×4) surfaces. Furthermore, our STM images lead us to rule out previously proposed models for both the Sb-induced (2×4) and clean GaAs(001)- (4×2) reconstructions.

Clean GaAs(001)- (2×4) surfaces were prepared by thermally desorbing an As capping layer from a Si-doped ($1\times 10^{18}\text{-cm}^{-3}$) epilayer. Details of the molecular-beam epitaxy growth and decapping procedures are given elsewhere.^{6,7} Approximately 1 ML of Sb was deposited onto the (2×4) surface, which was held at room temperature (RT), by effusion from a Knudsen cell operated at 410°C .

The Sb-terminated surface was then annealed at temperatures in the $200\text{--}580^\circ\text{C}$ range, as described below. We use a commercially available tunneling microscope (W.A. Technology, Cambridge, U.K.) with electrochemically etched W tips cleaned by electron bombardment.

Following decapping and annealing at 450°C the GaAs(001) surface forms a (2×4) reconstruction. Filled-state STM images show that in our case the decapped⁷ and *in situ* grown (2×4) surfaces⁸ are structurally very similar. The (2×4) periodicity is due to a regular array of As dimers and missing dimers (two missing dimers per unit cell (Ref. 8) [Fig. 1(c)]. Figure 1(a) shows an STM image of the surface that is formed following deposition of approximately 1 ML of Sb on GaAs(001)- (2×4) with subsequent annealing at 200°C . (There was little difference between STM images taken directly after RT Sb adsorption and those taken following the 200°C anneal.) Rows running along the $[\bar{1}10]$ direction with a 16-\AA spacing are clearly visible. A higher magnification scan, as shown in Fig. 1(b), reveals that each bright row has a dark "node" along its center. Islands having the same row structure and a height of approximately 2.8 \AA [the GaAs(001) step height] are also observed. These islands arise from the morphology of the initial clean (2×4) surface before Sb deposition.⁶ No islanding of the first ML of Sb occurs, in contrast to Sb adsorption on GaAs(111)*B*- (2×2) , where the growth mode is Volmer-Weber.⁹

RHEED and PES studies⁴ have shown that for annealing in the $200\text{--}360^\circ\text{C}$ range, the Sb-terminated GaAs(001) surface exhibits a (1×4) reconstruction for which there is no Sb-Ga bonding but both Sb-Sb and Sb-As bonding states exist. The observation of rows with a 16-\AA spacing along the $[\bar{1}10]$ direction is thus consistent with the ordering implied by RHEED [$a(100) = a_0/\sqrt{2} = 4\text{ \AA}$]. Considering the PES and STM measurements together leads us to propose a model for the structure exhibiting (1×4) symmetry in RHEED as shown in Fig. 1(d). We suggest that the As-As dimers of the clean GaAs(001)- (2×4) structure [Fig. 1(c)] are broken by adsorbed Sb, which itself subsequently dimerizes. While we

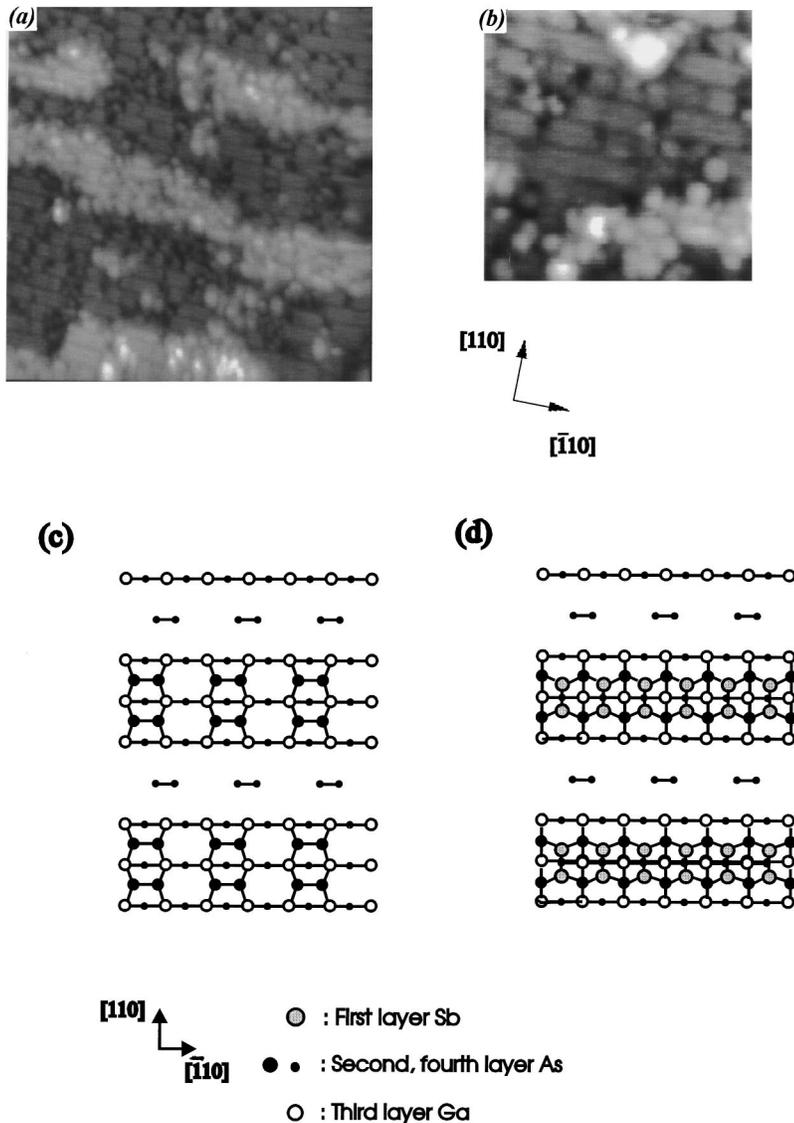


FIG. 1. (a) A 380×380 - \AA^2 image of the GaAs(001):Sb-(1×4) surface resulting from deposition of approximately 1 ML of Sb with subsequent annealing at 200°C . (b) A higher magnification scan (150×150 \AA^2) showing the presence of a dark “node” in the rows. Scan parameters for these and subsequent images are -3.5 V and 100 pA. (c) A ball-and-stick model of the clean GaAs(001)-(2×4) surface. (d) Our proposed structural model for the reconstruction formed after annealing the Sb-terminated GaAs(001) surface at 200°C . We cannot determine directly from the STM images if the third-layer As dimers of the GaAs(001)-(2×4) reconstruction are broken by Sb. However, considering the (1×4) RHEED pattern, this is likely to occur.

cannot conclusively determine from photoemission and STM data whether the third-layer As dimers are also broken by adsorbed Sb, the lack of a ($2 \times$) periodicity in the RHEED pattern suggests that this occurs. If either some or all of the GaAs(001)- 2×4 third-layer As dimers are broken the ($2 \times$) periodicity will be removed. Thus, each first-layer Sb atom is bonded to two As atoms and one other Sb atom and has a lone pair dangling bond. The node observed along the center of the rows may be associated with the lower energy of the Sb-Sb dimer bond compared to the Sb lone pair dangling bonds. The separation of the bright features within a row, which we argue correspond to Sb lone pairs, is approximately 5\AA . This is much greater than the dimer bond length expected from the covalent radius of Sb (2.72\AA);¹⁰ however, we would expect the peaks in the Sb lone pair charge density to be shifted away from the Sb atom positions.

Following annealing in the 360 – 440°C range, the RHEED pattern from an Sb-terminated surface indicates a (1×3) reconstruction.⁴ Figure 2 shows an STM image of the surface after annealing at 400°C . There is a significant lack of long-range order with short chains distributed across the surface. For regions where the chains run in the $[\bar{1}10]$ direction the spacing between neighboring chains is approxi-

mately 12\AA , corresponding to a $3 \times$ periodicity. Our data are somewhat similar to STM images of the InSb(100)-(1×3) surface;¹¹ however, in our case the chains do not predominantly run along the $[\bar{1}10]$ direction but exhibit considerably more anisotropy. The high degree of disorder precludes the proposal of a well-defined structure model for the GaAs(001):Sb-(1×3) phase.

Annealing of the Sb-terminated surface at a temperature between 440 and 560°C induces a change in surface structure to a (2×4) reconstruction (as observed by RHEED).⁴ Core-level PES data show that for this reconstruction all As atoms are in a bulk environment and that only Sb-Ga bonds exist at the surface.⁴ This result indicates a replacement of surface As by Sb. We have observed a similar replacement of As by Sb on the GaAs(111)*B* surface.¹² Our STM data, taken following annealing of the surface at 480°C , confirm the change in surface reconstruction from (1×3) to (2×4). 16 - \AA spaced rows running along the $[\bar{1}10]$ direction are clearly observed in the filled-state image shown in Fig. 3(a). In this scan features within the rows having an 8 - \AA or $2 \times$ periodicity along the $[\bar{1}10]$ direction are also clearly resolved. These features arise from symmetric Sb-Sb dimers in the uppermost surface layer whose dimer bond lengths have

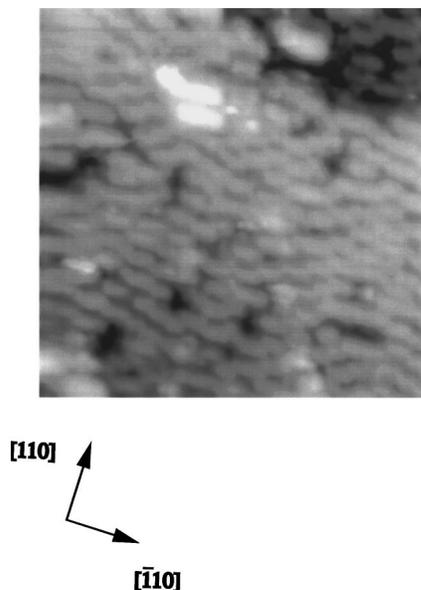


FIG. 2. 230×230 - \AA^2 image of the (1×3) reconstruction formed by annealing the Sb-terminated surface at a temperature of 400°C . The reconstruction has little long-range order, consisting of short Sb chains distributed across the surface.

been previously investigated using XSW (Ref. 5) and found to be $2.95 \pm 0.05 \text{\AA}$. The dark rows running along the $[\bar{1}10]$ direction may be associated with missing Sb dimers. We observe a difference in the number of missing dimers per unit cell, although the unit cell retains a (2×4) periodicity.

There are a number of notable differences between the clean As-terminated and Sb-induced (2×4) reconstructions. Unit cells consisting of a *single* Sb-Sb dimer are the predominant structure, as opposed to the two dimer unit cells of the clean GaAs(001)- (2×4) surface. The predominance of single Sb dimer unit cells is observed following annealing at temperatures in the entire 450 – 560°C range over which the (2×4) unit cell is present. There are in fact two single-Sb-dimer unit cells, depending on the placement of the dimer within the cell. Interestingly, there appears to be some correlation between neighboring unit cells along the $[\bar{1}10]$ direction in that we rarely observe extended “zigzag” patterns of single dimers. Unit cells consisting of three Sb-Sb dimers were previously proposed to explain the Sb-induced (2×4) periodicity.⁴ Our data are not consistent with this model. Our proposed structure model for the single-Sb-dimer unit cell is shown in Fig. 4.

At the single dimer sites features intermediate in apparent height between the Sb dimers and the missing dimer rows are resolved [Fig. 3(b)] and arise from tunneling from second-layer Ga atoms. The profile [Fig. 3(c)] along the line *AB* in the figure illustrates that these Ga-related features are $\sim 1.3 \text{\AA}$ “lower” than the Sb dimers. Variations in filled-state charge density will cause this value to differ from the $1.8\text{-}\text{\AA}$ separation of the first Sb layer and second Ga layer deduced in a recent x-ray standing-wave study.⁵ Interestingly, as also observed on the clean GaAs(001)- (2×4) surface, we do not resolve Ga-related features for two dimer unit cells. There is also a significantly lower density of kink sites on the GaAs(001):Sb- (2×4) , as compared to the clean As-terminated (2×4) surface.

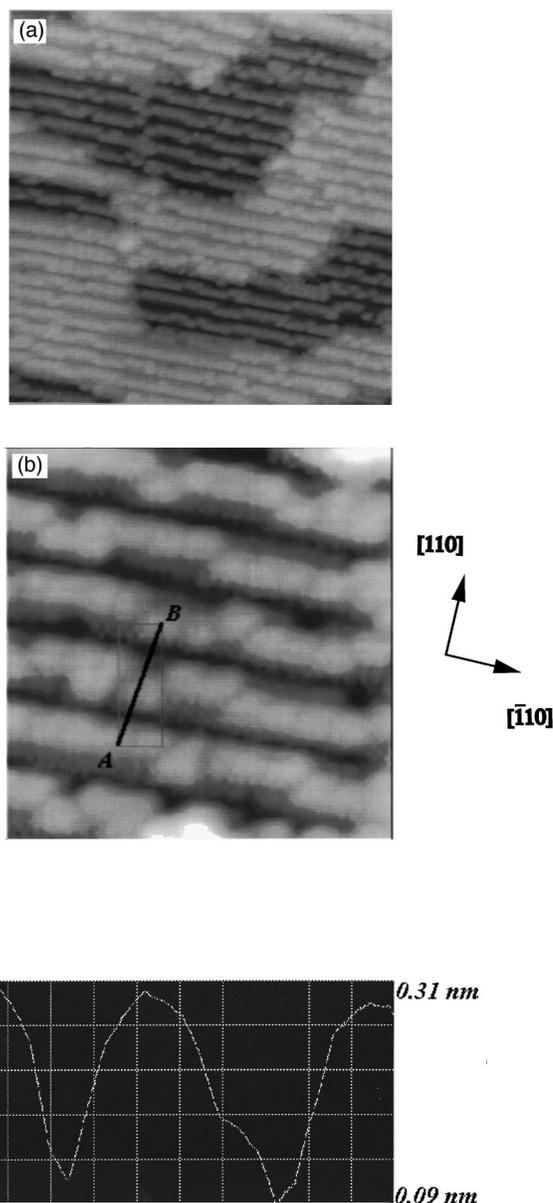


FIG. 3. (a) The Sb-induced GaAs(001)- (2×4) structure is shown in this 310×310 - \AA^2 image. The unit cells consist predominantly of one Sb dimer and three missing dimers. (b) A 165×165 - \AA^2 image where features due to second-layer Ga are resolved. (c) A scan profile taken along the line *AB* in (b) shows that the Ga features appear 1.3\AA lower than the first-layer Sb.

The electron counting rule¹³ is commonly used to predict possible reconstructed structures for polar semiconductor surfaces. This model dictates that III-V surfaces, including those with adsorbates, will reconstruct so that all group-V dangling bonds are filled and all group-III dangling bonds are empty. For our proposed model of the single-Sb-dimer (2×4) unit cell, it is possible to satisfy electron counting by transferring electrons from Ga to Sb dangling bonds. However, this would imply that Ga dangling bonds would not be imaged in a filled-state topograph, contrary to our experimental results.

The final annealing cycle (580°C) gives rise to a complete change in surface structure and bonding due to the desorption of the Sb overlayer.⁴ Figure 5 shows a comparison

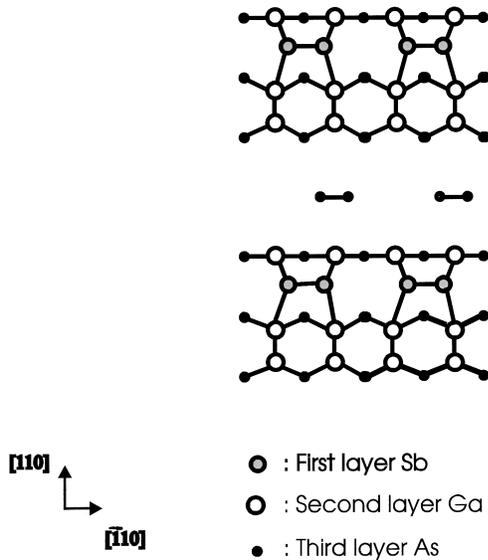


FIG. 4. A proposed structural model for the GaAs(001):Sb(2 \times 4) unit cell.

of the clean GaAs(001)-(4 \times 2) reconstruction and the structure resulting from annealing the Sb-terminated surface at a temperature above the Sb desorption point. The dominant features in both these images are the 16-Å spaced rows running along the [110] direction. In agreement with this, Maeda, Watanabe, and Oshima⁴ have reported the observation of a (4 \times 2) RHEED pattern following annealing of an Sb-terminated GaAs(001) surface at temperatures in excess of 560 °C. Skala *et al.*¹⁴ have proposed that for clean GaAs(001) these rows correspond to first-layer As dimers, contrary to earlier reports that determined that the (4 \times 2) surface was Ga rich. As mentioned above, the core-level photoemission data presented by Maeda, Watanabe, and Oshima⁴ indicated that for the Sb-induced (2 \times 4) reconstruc-

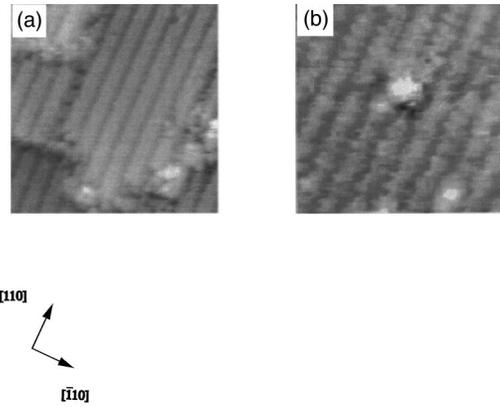


FIG. 5. (a) The (4 \times 2) reconstruction of the clean decapped GaAs(001) surface (170 \times 170 Å²). (b) The surface structure resulting from desorption of the Sb overlayer from the GaAs(001) surface (140 \times 140 Å²). 16-Å spaced rows running along the [110] direction are clearly visible in both images.

tion all the surface As was replaced by Sb. Thermal desorption of the Sb overlayer must therefore yield a *Ga-rich surface*. Thus, the model for the (4 \times 2) reconstruction proposed by Skala *et al.*¹⁴ consisting of rows of first-layer As and second-layer Ga dimers may be ruled out.

In conclusion, we have used STM to provide real-space images of the (1 \times 4), (1 \times 3), and (2 \times 4) reconstructions resulting from the interaction of Sb with a GaAs(001)-(2 \times 4) surface. Considerable differences exist in the structure and ordering of the (2 \times 4) unit cells on the Sb-terminated and clean GaAs(001) surfaces. Following thermal desorption of the Sb overlayer, a (4 \times 2) reconstruction is observed which is a Ga-rich phase, contrary to a previous report.

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