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Double chain structures on the Sb-terminated GaAs(111)*B* surface

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The interaction of Sb with the GaAs(111)*B*-(2×2) surface has been investigated using scanning tunneling microscopy. Pairs of parallel Sb lines oriented along the ⟨110⟩ directions and separated by three lattice constants are observed. Adjacent pairs are separated by p rows of atoms where p varies between two and five lattice constants. Between the line pairs we observe a pattern of Sb trimers with periodicity m parallel to the chains between three and seven lattice constants, which is determined by the value of p. The predominant unit cell corresponds to a 3×8 reconstruction. The local ordering can be understood in terms of electron counting.

An important property that can be used to characterize the physics and chemistry of semiconductor surfaces is their interaction with chemisorbed species. These studies yield information which is of value for related technologies, for example, molecular-beam epitaxy, and also contributes to a fundamental understanding of the properties of surfaces. For the III-V compound semiconductors the most widely studied surfaces are (110), which is the natural cleave plane, and (100), which is the most common choice for epitaxial growth. However, there is now considerable interest in heterostructures grown by molecular-beam epitaxy on III-V substrates oriented in the (111) direction since a piezoelectric field may be induced in strained layers for this orientation.[1] In addition Golding *et al.* have recently shown that epitaxial growth of semimetallic antimony on (111)-oriented GaSb is possible.[2] To date there have been few studies of III-V {111} surfaces and even fewer related to their interaction with absorbates.

In this paper we describe the interaction of Sb monolayers and submonolayers with the As-terminated GaAs(111)*B* surface. A family of complex reconstructions are observed that, to our knowledge, are qualitatively different from any other reported surface structures. The unit cells of every member of this family of reconstructions incorporate two parallel chains which are separated by three lattice constants. Adjacent chain pairs are separated by p rows of atoms. The value of p varies across the surface and may correspond to 2, 3 (the most common value), 4, or 5 lattice constants. In between adjacent chain pairs Sb trimers are observed with several different patterns of local order.

The clean GaAs(111)*B* surfaces were prepared by removing an As capping layer from a 500-nm GaAs buffer layer, doped with Si at a concentration of 2×10^{18} cm^{-3} grown by molecular-beam epitaxy.[3] Removal of the As cap was carried out in an ultrahigh vacuum (UHV) chamber (base pressure 6×10^{-11} Torr) by annealing in the range 300–375 °C for times ranging from 10 to 60 min.

Sb was deposited from an effusion cell calibrated using a quartz crystal thickness monitor. The pressure remained below 6×10^{-10} Torr during Sb evaporation. The GaAs was held at room temperature during deposition. The scanning tunneling microscope (STM) was provided commercially by W. A. Technology, Cambridge, U.K. and is situated in an adjacent UHV chamber. The STM tips were electrochemically etched from tungsten wire and heated by electron bombardment to approximately 1600 °C, for 5–10 min.

A clean GaAs surface prepared as above undergoes a (2×2) reconstruction.[4] After deposition of submonolayer coverages of Sb much of the surface retains this 2×2 reconstruction (see Fig. 1). The topographic maxima in STM images of the clean surface are identified as As trimers chemisorbed on an underlying unreconstructed full As layer. In practice several domains of the (2×2) reconstruction separated by surface defects are observed. In agreement with Fu *et al.*[5] we find that prior to evaporation of Sb the Fermi level is pinned 0.5–0.6 eV from the valence-band maximum.

After depositing 0.2 ML of Sb and annealing the sample at 370 °C the surface morphology is found to change in localized regions 10–20 nm wide, while the 2×2 As trimer reconstruction is still observed over most of the surface. Fig-

FIG. 1. A 21-nm^2 STM image (sample bias, $V=-1.8$ V, $I=-100$ pA) of GaAs(111)*B* after evaporation of 0.2 ML of Sb and annealing to 370 °C.

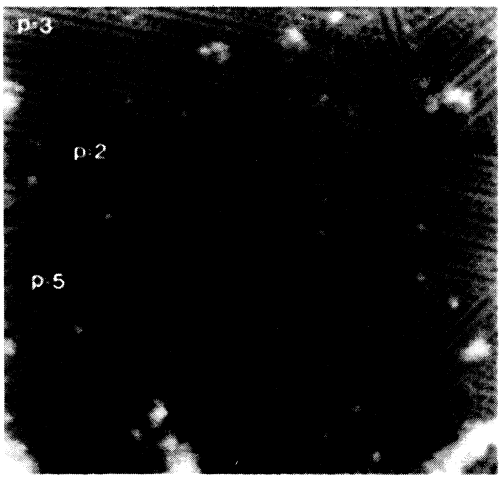

FIG. 2. A 40-nm^2 STM image ($V=-3$ V, $I=-100$ pA) of GaAs(111)B after deposition of 3 ML of Sb and annealing at 375 °C. Areas where adjacent pairs are separated by $p=2$, 3, and 5 lattice constants are identified.

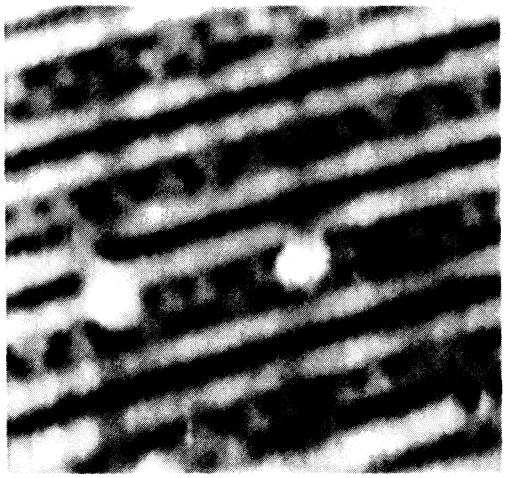

FIG. 3. A 10-nm^2 image ($V=-3$ V, $I=-100$ pA) of a sample prepared as in Fig. 2. The area includes chain pairs separated by $p=2$, 3, and 5 lattice constants. Note that the individual atoms of trimers in H_3 sites are resolved—see trimer identified by arrow.

ure 1 shows an STM image of a boundary between an unchanged part of the surface (upper and left part of image) and an area which has been modified by the presence of the antimony (lower-right part of the image). Part of the boundary between modified and unmodified areas is formed by two parallel lines (which we refer to as a chain pair) running in one of the ⟨110⟩ directions. The separation of the lines along one of the principal axes is 1.18 nm, equivalent to $3\times$ the separation of lattice points as compared with unreconstructed GaAs.

Figure 1 shows a difference in apparent height between the upper and lower halves of the image, i.e., regions above and below the chain pair. The region appearing higher in the filled state topograph (lower-right part of Fig. 1) also exhibits a higher degree of surface disorder. Empty- and filled-state images show topographic peaks in identical positions, with the modified region appearing higher in both sets of images. The apparent height difference, ~ 0.11 nm ($\pm 10\%$), is therefore principally topographic, rather than electronic, in origin.

We believe that the surface morphology is due to Sb diffusing and forming islands. Annealing causes the Sb adhering to the surface to react and displace the chemisorbed As trimers, while the rest of the Sb in an island is desorbed. This is supported by a comparison of modifications to the surface produced by annealing the sample at temperatures between 100–375 °C for submonolayer coverages. At low annealing temperatures (and for no annealing) we observe islands of adsorbate with typical diameter 10–20 nm between which the 2×2 reconstruction characteristic of the clean GaAs is observed. A replacment of As by Sb has also been reported by Maeda, Watanabe, and Oshima[6] for GaAs(100).

Figure 2 shows an STM image of the surface taken after deposition of 3.0 ML of Sb and subsequent annealing at 375 °C. For this coverage of Sb the image in Fig. 2 is representative of any part of the sample surface and we do not observe any remaining unreacted areas of (2×2) As-terminated GaAs. Figure 2 shows chain pairs (similar to those in Fig. 1) running in each of the ⟨110⟩ directions with lengths up to 50 nm. No features could be resolved within the chains for tunneling biases of -3 to $+3$ V and currents of 0.1 to 1 nA.

The spacing of the constituent lines of a chain pair is always found to be 3 lattice constants, but the separation of adjacent chain pairs varies across the surface. Areas with separation $p=2$, 3, and 5 rows of atoms are identified in Fig. 2. The most common separation is $p=3$, followed by $p=2$. Relatively small areas with $p=5$ are observed and an even smaller proportion with $p=4$. Between adjacent chain pairs there is a periodic arrangement of topographic maxima with varying degrees of order. For example, see the zigzag arrangement in the top left of Fig. 2 for $p=3$. The periodicity m (in units of the lattice constant) of these patterns parallel to the chains depends on the value of p.

A higher magnification image of the surface is shown in Fig. 3 which shows that the topographic features between the chain pairs are triangular. Furthermore we are able to resolve structure within these triangular features. This is seen most clearly in the triangles which point down in Fig. 3, for example, the one identified by an arrow. Our images therefore imply that these features correspond to Sb trimers in which each Sb atom is bonded to the two other Sb atoms in the trimer and one As atom in the top layer of the GaAs (the reason why we believe this to be an As atom rather an Sb atom which has displaced As is given below). The conjecture that they are Sb rather than As trimers is supported by the fact that we (in common with other groups) are unable to resolve the constituent atoms of the As trimers formed on the (2×2) clean As-terminated surface. Note that our images show that for $p=2$ the Sb trimers may sit on either the T_4 or H_3 sites corresponding to triangles pointing either up or down in Fig. 4. The separation between trimers pointing up and down is equal to 2.5 lattice constants. This is in contrast to both (i) As trimers on the (2×2) reconstructed GaAs surface and (ii) the Sb trimers between chains separated by $p>2$ lattice constants. For these cases it has been established that the trimers all sit on the T_4 site by (i) calculations (see

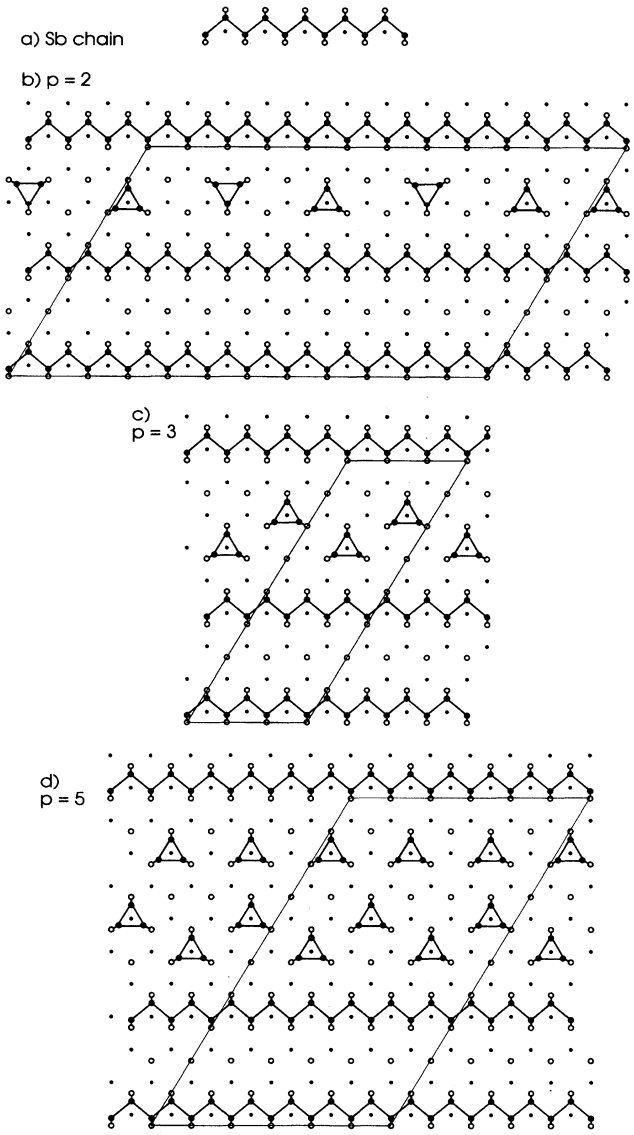

FIG. 4. Bonding configurations for the Sb-terminated GaAs(111)B surface. Large filled circles represent Sb, open circles As, and small filled circles Ga. Bonds between surface As atoms and the chemisorbed Sb are represented by straight lines: (a) The bonding for a chain; (b) bonding configuration of (12×7) unit cell for $p=2$; (c) bonding configuration of (3×8) unit cell for $p=3$; (d) bonding configuration of (6×10) unit cell for $p=5$.

Ref. 4 for As-terminated GaAs) and (ii) comparison of the orientation of trimers in reacted and unreacted areas of the sample for submonolayer coverages of Sb.

We now consider the bonding arrangement of the lines forming the chain pairs. McGinley *et al.*[7] have observed that following the absorption of 3 ML of Sb and annealing at 350 °C the Sb $4d$ core-level photoemission spectrum consisted of a single well-resolved spin-orbit split doublet. Their results clearly show that Sb resides at the surface in only one bonding configuration implying (i) that Sb has not displaced As at any level lower than the trimer layer since in this case Sb would be bonded to subsurface Ga atoms and (ii) that all Sb atoms at the surface are bonded to two other Sb atoms and one As atom as they are in the trimer. This leads us to propose a structure for the lines which make up the chain pair which is similar to that proposed for the (2×1) reconstruction on the Sb-terminated Si(111) surface.[8] A short section of such a line is shown in Fig. 4(a). A chain pair consists of two such lines separated by 3 lattice constants.

We now consider the possible unit cells which may be constructed from a chain pair plus trimers. To account for the details of the periodicities m of the various patterns parallel to the lines we assume that the reconstruction (and relationship between p and m) is driven by the requirement that all bonding and lone pair orbitals of group-V atoms are filled, and that all states at the surface with higher energy are unoccupied. This is equivalent to the electron counting model described by Pashley[9] (see also Ref. 4).

We denote by l the number of trimers per unit cell. In the unreconstructed GaAs(111)B surface there are on average $\frac{5}{4}$ of electron associated with each As atom. Those As atoms which bond to Sb atoms relinquish $\frac{1}{4}$ electron which they donate to As atoms which are not bonded to Sb. According to the electron counting model the only arrangements of Sb atoms which are permitted are those in which the total number of electrons relinquished by As atoms bonded to Sb are exactly enough, but no more, to fill the lone pair orbital of each unbonded As atom at the surface. The number of As atoms per reconstructed unit cell $=m(p+5)$ and the number of As atoms which are bonded to Sb atoms $=(3l+4m)$. To satisfy electron counting the following condition must be satisfied:

$$\{3l+4m\}/4=3\{m(p+5)-3l-4m\}/4.$$

This gives a relationship between m and l. The lowest integer values of m and l for given p which satisfy the above equations are as follows:

$$\begin{aligned} p=2:&\quad m=12,\quad l=5;\\ p=3:&\quad m=3,\quad l=2;\\ p=4:&\quad m=12,\quad l=11;\\ p=5:&\quad m=6,\quad l=7. \end{aligned}$$

To summarize, this gives the expected periodicity m and number of trimers l for a given chain pair separation p. If any particular separation p were extended over a large area the resulting reconstruction would be $m\times(p+5)$.

In Figs. 4(b)–4(d) we show atomic configurations for unit cells for $p=2$, 3, and 5, respectively. For $p=3$ [see Fig. 4(c)] $m=3$ and $l=2$ satisfy the constraints imposed by electron counting. The reconstruction consists of a pair of parallel lines together with a zigzag pattern of Sb trimers sitting in T_4 sites which is equivalent to the area identified in the top left of Fig. 2. Note that the observed periodicity of the trimer pattern parallel to the lines is $3\times$ in agreement with the atomic configuration in Fig. 4(c). This unit cell is equivalent to a (3×8) reconstruction. However it is clear that the surfaces that are shown in our STM images have a substantial amount of disorder and the zigzag of trimers is broken up by trimer vacancies and trimers sitting in positions which are out of phase with the unit cell.

For $p=2$ the reconstruction is more complex. The pattern of trimers between adjacent pairs of lines must satisfy the requirement that there are 5 trimers per 12 lattice constants along the lines. Figure 4(b) shows a unit cell which consists of 3 trimers bonded at T_4 sites and 2 at H_3 sites and satisfies these constraints. The separation between trimers at T_4 and H_3 sites is 2.5 lattice constants, and there is also one pair of trimers each in T_4 sites and separated by 2 lattice constants. However we are unable to identify a $12\times$ unit cell in our images. The most regular sequence in Figs. 2 and 3 for $p=2$ shows trimers alternating between T_4 and H_3 sites, i.e., pointing alternately up and down, separated by 2.5 lattice constants. Note that the average separation between trimers in the proposed unit cell is $\frac{12}{5}=2.4$, very close to the observed spacing of trimers, and that an alternative means of satisfying electron counting would be to have trimers in a T_4, H_3,T_4,H_3,T_4,H_3, . . . sequence separated by 2.5 lattice constants together with a defect corresponding to a trimer in the wrong orientation which occurs on average (but not necessarily regularly) every 4 trimers. Note that such a defect is observed in Fig. 3 immediately to the left of the arrow. Within this model we can therefore account for our experimental observations which correspond to a periodicity parallel to the lines of $m=5$ with some degree of disorder.

The smallest possible unit cell for $p=5$ which satisfies electron counting corresponds to (6×10) local ordering [see Fig. 4(d)]. The trimers sit on T_4 sites and are arranged as a combination of a line of regularly spaced trimers (separation 2 lattice constants) and a zigzag of trimers. Small regions with this reconstruction are observed in our images—see, for example, the area immediately above the legend "$p=5$" on Fig. 2—but rarely persist for more than two unit cells.

Our results imply that it is more favorable energetically for Sb to be bonded in chains, whereas the trimer configuration is more stable for As. This may be partially understood in terms of the bond lengths and angles for bulk and molecular forms of Sb and As. Both elements form a tetrahedral molecule with bond angle 60°, whereas in the solid crystalline form the bond angle is larger, ~96.5° for both elements. The bond lengths in the crystal are $d_{Sb}=0.29$ nm and $d_{As}=0.25$ nm for Sb and As, respectively. If this were the bond length between atoms in the lines shown in Fig. 4(a) then the bond angles for Sb would be $\{180°-2\cos^{-1}(d_{As-As}/2d_{Sb})\}=87°$, where $d_{As-As}=0.4$ nm is the spacing between As atoms on the unreconstructed surface. The corresponding figure for As is 106°. Thus the angle for Sb falls within the range found in naturally occurring compounds, whereas that for As is substantially larger.

For all cases except a spacing $p=2$ we observe Sb trimers at a T_4 site, implying that this is the lowest energy configuration. However, for $p=2$ trimers sit at H_3 sites. An alternative packing which could still satisfy electron counting would be trimers all at T_4 sites but separated by 2, 3, 2, 3, 2 lattice constants. Such a configuration is never seen in our images which implies that packing the trimers closer together increases their energy, presumably due to the repulsion of electrons in lone pair orbitals, by an amount that is greater than the difference in binding energy for trimers at T_4 and H_3 sites. For As trimers this difference has been calculated by Biegelsen *et al.*[4] and found to be ~60 meV.

In conclusion we have observed a qualitatively new family of surface reconstructions on the Sb-terminated GaAs(111)*B* surface. These reconstructions appear to be driven by the formation of Sb chains. Since a uniform coverage of these chains would not satisfy electron counting a more complex reconstruction evolves in which Sb chains and trimers coexist on the surface.

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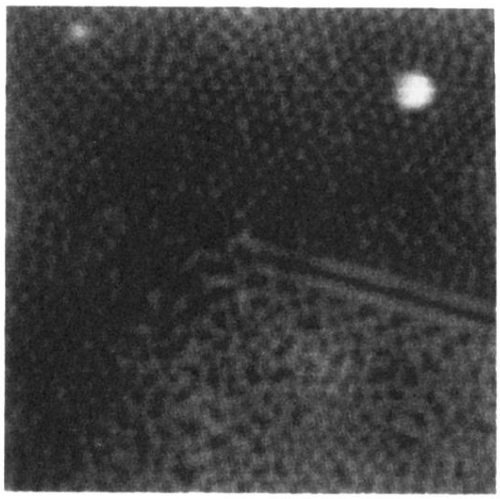

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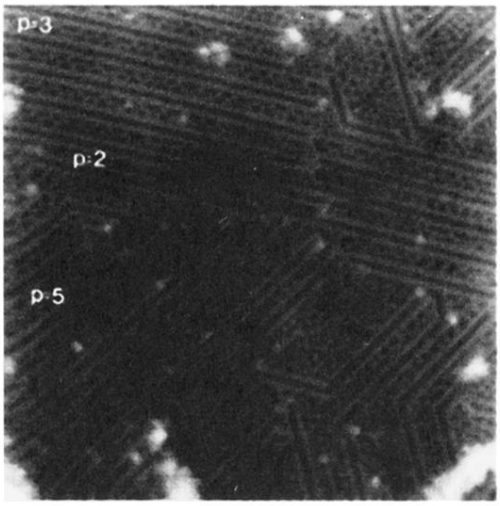
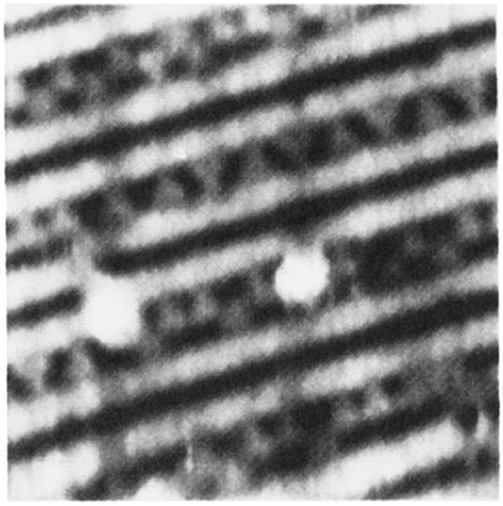


FIG. 2. A 40-nm^2 STM image ($V=-3$ V, $I=-100$ pA) of GaAs(111)B after deposition of 3 ML of Sb and annealing at 375 °C. Areas where adjacent pairs are separated by $p=2$, 3, and 5 lattice constants are identified.



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