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Bismuth-induced restructuring of the GaSb(110) surface

T. van Gemmeren, L. Lottermoser, G. Falkenberg, L. Seehofer, and R. L. Johnson
II. Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Federal Republic of Germany

L. Gavioli and C. Mariani
Dipartimento di Fisica, Università di Modena, via G. Campi 213/A, I-41100 Modena, Italy

R. Feidenhans'l, E. Landemark, D. Smilgies, and M. Nielsen
Risø National Laboratory, DK-4000 Roskilde, Denmark

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The structure of the GaSb(110)(1×2)-Bi reconstruction has been solved using surface x-ray diffraction, scanning tunneling microscopy, and photoelectron spectroscopy. The ideal GaSb(110) surface is terminated with zigzag chains of anions and cations running in the $[1\bar{1}0]$ direction. In the Bi-induced (1×2) reconstruction we find that every second zigzag chain in the uppermost substrate layer is missing. The reconstructed surface is terminated with a full monolayer of Bi atoms which also form zigzag chains. The Bi atoms in the chains bond alternately to the first and second layer substrate atoms and the Bi chains are inclined at 34° to the (110) plane. [S0163-1829(97)03335-3]

Metal-semiconductor interfaces are of considerable interest for both fundamental and technological reasons. Most vapor-deposited metals react with III-V semiconductors to form complex, nonstoichiometric interfaces, however, it is generally believed that the semimetals Sb and Bi form nonreactive ordered interfaces.[1] Group-V metals on III-V semiconductors are frequently regarded as examples of ideal adsorbate-semiconductor heterojunctions. In this paper we present a structural model which demonstrates that this simple picture is not universally true since, as we shall show, bismuth can induce significant restructuring of the GaSb(110) surface.

The deposition of one monolayer (ML) of Sb or Bi on most III-V(110) semiconductor surfaces at room temperature results in the formation of a (1×1) reconstruction. There is now a general consensus in favor of the epitaxial continued layer structure (ECLS) for this reconstruction originally propose by Skeath *et al.*[2] In this model the surface is terminated by a full monolayer of adsorbate atoms which form zigzag chains running in the $[1\bar{1}0]$ direction. The adsorbate atoms bond alternately to the anions and cations which move back towards their bulk positions, i.e., the surface relaxation of the first substrate layer is reduced. The Sb, or Bi, atoms are located at positions similar to those that the anions and cations would occupy if the crystal were continued. In the ECLS the surface dangling bonds are fully saturated. The bonding configuration of the adsorbate atoms is characterized by p^2 bonding within the adsorbate chains and a p_z backbond which interacts with the sp^3 hybridized orbitals of the substrate.[3] This intuitively appealing picture, however, does not explain why the 1×1 structures of Bi on GaSb(110) and InAs(110) are metastable and transform into a stable (1×2) structure upon heating, nor why Bi on InSb(110) only forms a (1×2) reconstruction.[1]

The (1×1) and (1×2) structures have significantly different electronic properties,[5,6] which until now was thought to arise from different atomic arrangements in the Bi layer. Here we show that the transition from the metastable (1×1) phase to the stable (1×2) phase of Bi on GaSb(110) involves a major restructuring of the GaSb(110) substrate. On the basis of our investigations using synchrotron radiation photoelectron spectroscopy, scanning tunneling microscopy (STM), and surface x-ray diffraction (SXRD), we have been able to derive a structural model which explains all the experimental data available. We believe that the model may be widely applicable and should apply to the other (1×2) adsorbate-induced reconstructions on III-V(110) surfaces.

The preparation of the samples and the photoemission measurements were performed on the FLIPPER II beamline at the Hamburg synchrotron radiation laboratory (HASYLAB). For the photoemission measurements small p-type (1.2×10^{17} cm^{-3}) GaSb(110) surfaces were prepared by cleaving. For the STM and SXRD measurements the surfaces were prepared by ion bombardment and annealing. Bi films with coverages between 1 and 9 ML (1 ML corresponds to 7.6×10^{14} atoms/cm^2) were deposited on the surface. The (1×2) structures were prepared by slowly heating the samples to sequentially higher temperatures to ensure that equilibrium conditions were achieved. For annealing temperatures between 200–330 °C sharp (1×2) low-energy electron diffraction patterns were observed. For the STM and SXRD measurements the sample was transferred in a portable ultrahigh vacuum chamber to the STM apparatus or to the surface diffractometer on the wiggler beamline BW2 at HASYLAB. The SXRD measurements were performed at a glancing angle of 1° with an x-ray wavelength of 1.38 Å.

The photoemission results are summarized in Fig. 1 which shows background-corrected[7] energy distribution curves of electrons excited from Ga $3d$, Sb $4d$, and Bi $5d$ core levels. A photon energy of 80 eV was chosen to ensure high surface sensitivity and similar escape depth (∼4 Å) for the electrons from the Ga $3d$, Sb $4d$, and Bi $5d$ core levels. The overall resolution was typically 200 meV. A curve-fitting procedure using approximated Voigt functions was

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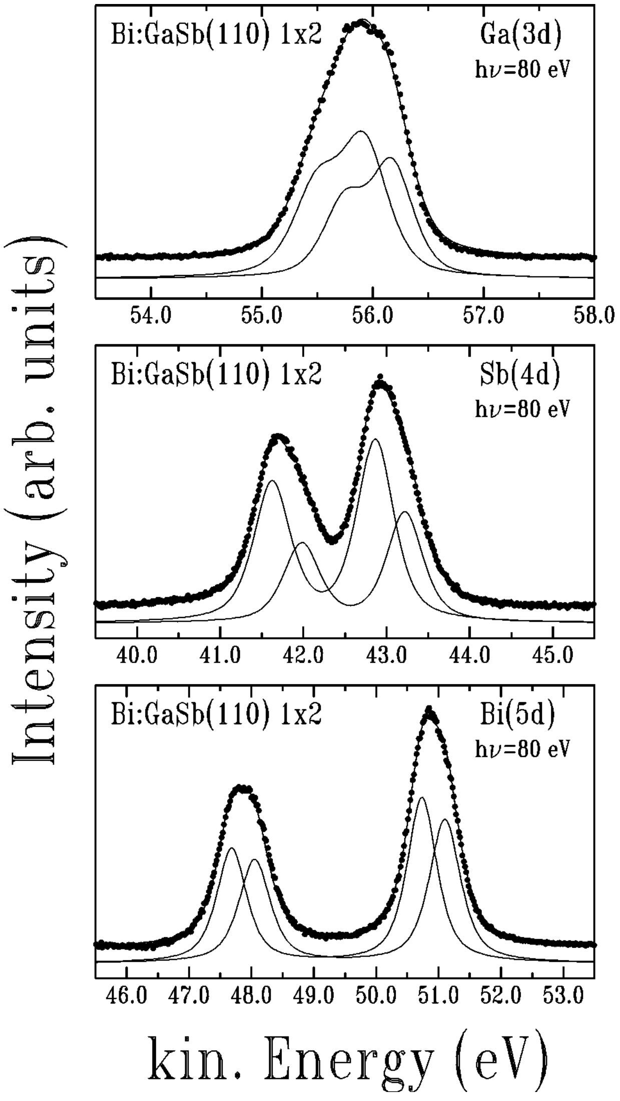

FIG. 1. Ga 3*d*, Sb 4*d*, and Bi 5*d* core-level spectra from the GaSb(110)-(1×2)-Bi reconstructed surface. The dots represent the experimental data; the solid lines show the different components and their sum.

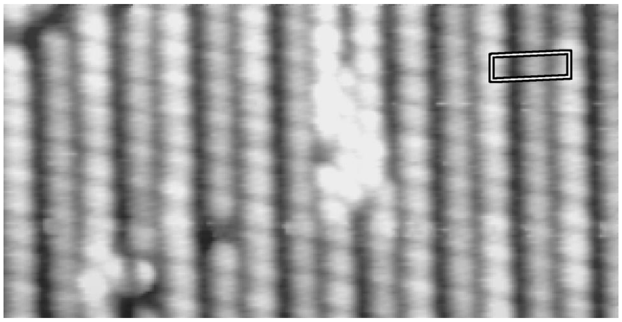

FIG. 2. STM image of a 100×60 Å^2 area of the (1×2) phase of Bi/GaSb(110) acquired at −1.2 V sample bias and 2.3 nA tunneling current. A (1×2) unit cell is outlined.

used to analyze the data.[7] The individual spin-orbit split Bi 5*d* peaks contain two components of similar intensity separated by 0.37 eV. In the (1×1) phase, the separation is only 0.32 eV—the higher kinetic component is associated with Bi-Ga bonds and the lower energy component with Bi-Sb bonds.[7] Angle-resolved valence-band photoemission studies indicate that the Bi chains remain intact during the (1×1)→(1×2) phase transition[6] so it is reasonable to make the same assignments for the Bi components in the (1×2) phase. The spectra from the substrate support this conclusion: In addition to the bulk component both the Ga 3*d* and Sb 4*d* spectra exhibit a component shifted by 0.25 and 0.35 eV to higher kinetic energy. The shifted components can be attributed to Ga and Sb atoms bonding to Bi. This is different from the (1×1) phase, where only a single component for both the Ga and the Sb bulk atoms and atoms bonding to Bi was observed.[7] Hence, the difference between the (1×1) and (1×2) phase must be more involved than just a reordering of the Bi chains, as suggested by McIlroy *et al.*[6] The nearly equal intensity ratios of the substrate components and of the two Bi components indicate that the surface contains a similar number of Bi-Ga and Bi-Sb bonds.

Figure 2 shows an STM image of the (1×2) phase recorded with −1.2 V sample bias and 2.3 nA tunneling current. The outlined area corresponds to a (1×2) unit cell with dimensions 4.3 ×12.2 Å^2. The shorter side of the unit cell is oriented in $[1\bar{1}0]$ direction while the longer side is parallel to the [001] direction. Each (1×2) unit contains two protrusions, namely, a bright protrusion located at the corner of the outlined unit cell, and a darker protrusion which is located in the center. The apparent height difference of the two protrusions is ~ 0.3 Å. Simply attributing the protrusions in the STM image to Bi atoms would be at variance with models which have zigzag chains of Bi atoms on the surface. The discrepancy can be removed if one assumes that the zigzag chains are tilted in opposite directions so that only every second Bi atom is visible in the STM image.

In order to determine the detailed atomic structure of the (1×2) reconstruction we performed extensive surface x-ray diffraction measurements. In total 98 fractional-order and 26 integer-order in-plane reflections were measured (of these 43 and 11 were nonequivalent) and in addition 12 fractional-order rods were collected. The structure factor intensities were obtained by correcting the measured integrated intensity with a Lorentz factor, for the variations in active sample area, and for polarization factors in the out-of-plane data.[8] All reflections are indexed with respect to a reciprocal surface unit cell given by $\mathbf{b}_1=[1\bar{1}0]_{\mathrm{bulk}}$, $\mathbf{b}_2=[001]_{\mathrm{bulk}}$ in the surface plane, and $\mathbf{b}_3=[110]_{\mathrm{bulk}}$ normal to the surface.

The in-plane fractional-order structure factors were used to calculate the Patterson function, shown as a contour plot in Fig. 3 (upper panel), which provides a map of the interatomic vectors within the surface unit cell of the (1×2) reconstruction projected onto the surface plane.[8] Apart from the peak at the origin, seven interatomic vectors are seen in the Patterson map. Four of these can easily be correlated with interatomic distances between the adsorbate atoms in the two Bi zigzag chains as can be seen from the structural model in Fig. 3 (middle panel). The other three strong peaks can be attributed to interatomic vectors between substrate atoms and Bi atoms. However, if the substrate layers were to maintain a (1×1) symmetry, the half-order reflections would have no scattering contributions from the substrate atoms. Which means that the fractional-order Patterson map should not include any interatomic vectors involving substrate atoms. Hence, to explain all the features in the Patterson map a significant reordering of the substrate must be included in the structural model. The substrate reconstruction was found using the electron density difference Fourier-synthesis technique which highlights the differences between the trial structure and the data.[8,9]

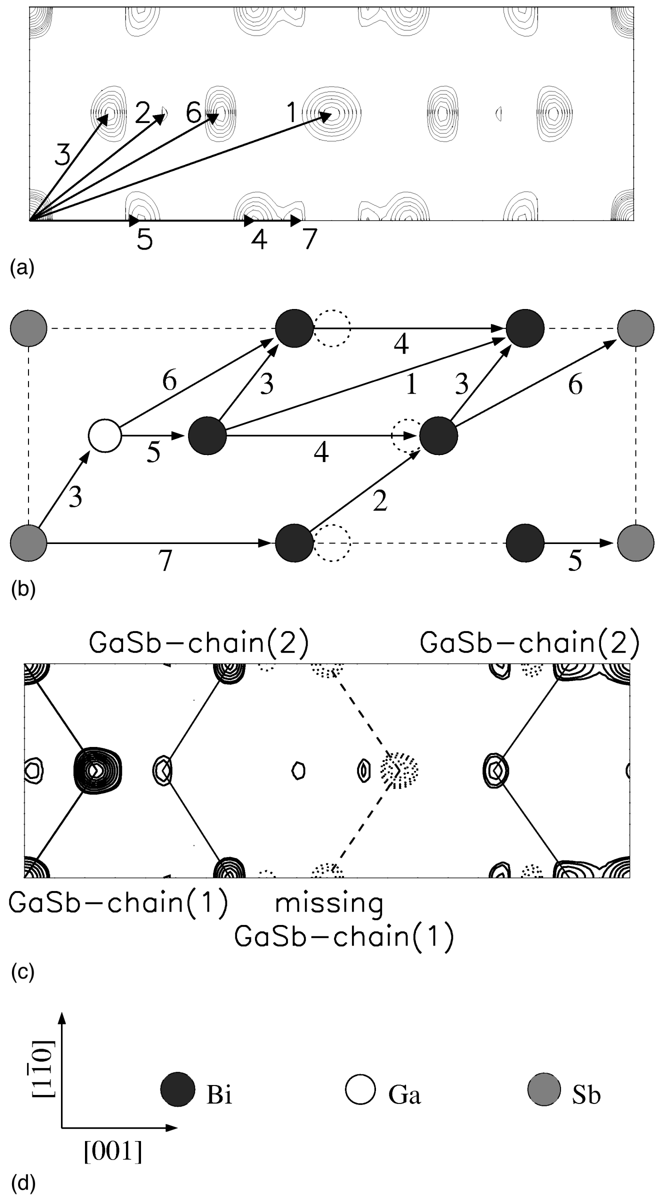

FIG. 3. Top panel: Contour map of the Patterson function of the GaSb(110)(1×2)-Bi reconstruction calculated from the in-plane fractional-order data. The seven positive maxima correspond to the seven interatomic vectors indicated the model of the surface unit cell shown in the middle panel. The dotted circles indicate the positions of the atoms in the missing substrate chain. Bottom panel: Electron density difference plot produced by subtracting the structure factors calculated for a trial model with only two Bi zigzag chains from the experimental in-plane data. Positive contours are marked with solid lines and the negative contours are dashed.

The lowest panel in Fig. 3 shows the electron density difference map $\Delta\rho$ calculated from the half-order in-plane structure factors and with phases derived from a starting model which only included two Bi zigzag chains. The positive peaks in the plot indicate electron density which is missing in the trial structural model and the negative peaks indicate excess electron density. The largest positive peaks in the difference map can be associated with atoms in three substrate zigzag chains which are indicated by solid lines in the electron density map. The dashed zigzag line in the electron density difference map indicates a substrate chain which is missing in the (1×2) reconstruction.

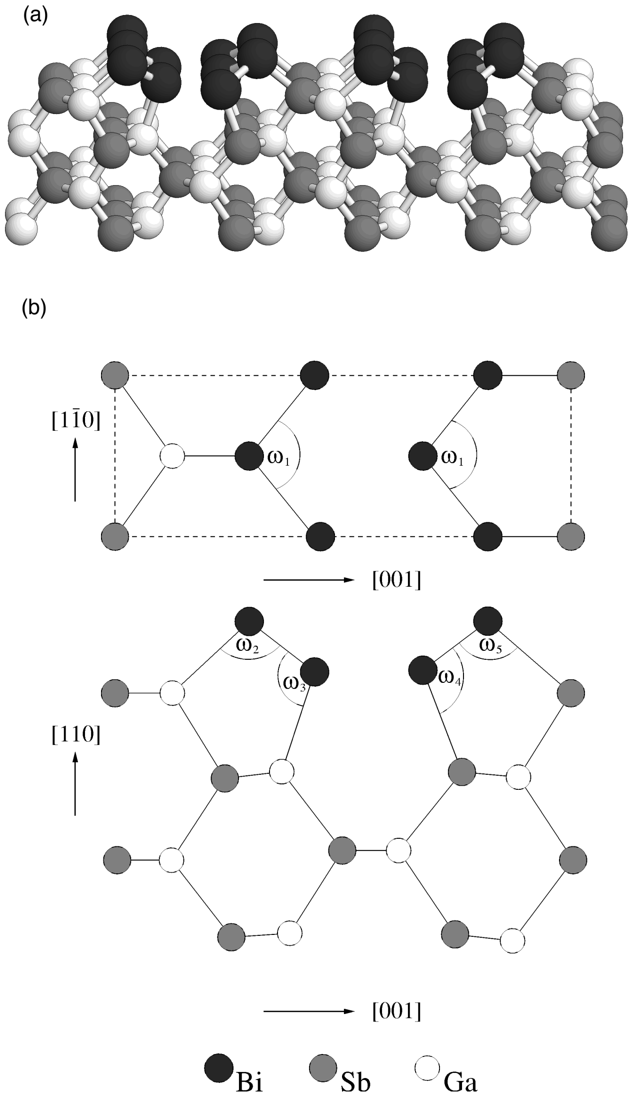

FIG. 4. (a) 3D ball and stick model of the GaSb(110)(1×2)-Bi reconstruction. (b) Top and side views of the final structural model of the GaSb(110)(1×2)-Bi surface.

The difference map provides clear evidence for a structural model in which every second substrate chain in the uppermost substrate layer is missing. The positive peaks in the electron difference plot can be associated with the atoms of one zigzag chain in the first substrate layer and to the atoms of two zigzag chains in the second substrate layer. Note that the missing substrate row structure reproduces all of the features in the Patterson map. The intensity variations along the fractional-order rods as a function of the momentum transfer Q_z perpendicular to the surface normal suggest that relaxations in deeper substrate layers have to be included in the structural model.[9]

A least-squares refinement was performed in the final data analysis. The positions of the atoms in the two Bi zigzag chains were refined allowing horizontal and vertical displacements down to the fourth substrate layer, while maintaining the substrate symmetry. An overall χ^2 of 1.4 was obtained for both the in-plane reflections and the fractional-order rods. In the final model, shown in Fig. 4(a) the two Bi zigzag chains of the (1×2) reconstruction are tilted towards the substrate missing row. The tilt angle, which is defined by the (110) plane and the plane of the Bi chains, was found to be $34°\pm3°$. The Bi intrachain bond angle ω_1 [see Fig. 4(b)] is $90°\pm2°$, which is closer to the p^2 bond angle within the Bi chains than in the (1×1)-phase where the angle was found to be $93°\pm2°$.[4] All the back bond angles ω_2-ω_5 of the tilted Bi chains to the substrate were found to be around 100° instead of 109° in the (1×1) phase (with an accuracy of $\pm1°$). The Bi-Ga bond lengths are 2.79 ± 0.08 and 2.87 ± 0.08 Å and the Bi-Sb bond lengths are 2.87 ± 0.07 and 2.96 ± 0.07 Å, which are close to the sums of the corresponding covalent radii (Bi 1.46 Å, Sb 1.4 Å, and Ga 1.26 Å). In the topmost substrate layer we determined Ga-Sb distances of 2.57 ± 0.06 and 2.77 ± 0.07 Å, corresponding to a 2.6% contraction and a 4.9% expansion relative to the bulk value of 2.64 Å.

The structure of the (1×2) phase of the Bi/GaSb(110) system presented in Fig. 4 with strongly tilted Bi zigzag chains bonded alternately to Ga atoms or Sb atoms in the first and second substrate layer is in agreement with the photoemission data. The Bi zigzag chains of the (1×1) phase remain intact on the surface during the transition from the (1×1) to the (1×2) phase. The changes in the photoemission spectra are not only due to charge transfer from the bonding of the Bi chains either to Ga or Sb atoms, but also the change in Madelung energy at the surface due to the strong tilt of the Bi chains. Electron counting reveals that all of the surface dangling bonds are fully saturated as confirmed by our resonant photoemission measurements.

The corrugation maxima in the STM images correspond to the top Bi atoms of the strongly tilted Bi chains. The apparent height difference of the maxima of ∼ 0.3 Å in Fig. 2 is not a geometrical effect because the heights of the atoms are the same to within the experimental uncertainty of 0.08 Å. The apparent height difference must be an electronic effect due to charge transfer in the Bi chains, as evidenced by the two different components in the Bi $5d$ core-level spectra and the fact that the apparent heights of the Bi atoms inverted when the sample bias polarity was changed in the STM measurements.

In conclusion, our results provide clear evidence that the GaSb(110)-(1×2)-Bi reconstruction consists of a monolayer coverage of tilted Bi zigzag chains running in the $[1\overline{1}0]$ direction with a missing-row structure in the uppermost substrate layer and concomitant subsurface relaxations. The Bi atoms are bonded to Ga and Sb atoms in both the first and second layers of the substrate. While the substrate bond angles remain at the values comparable to the (1×1) phase, the adsorbate bond angles in the (1×2) phase are closer to the ideal p^2 and p_z bond angles than in the (1×1) phase. Therefore, we propose that the formation of the reconstruction is driven by the very favorable bonding geometry in the adsorbate chains. This immediately explains why Bi on InSb(110) only forms a (1×2) reconstruction; the larger lattice constant of InSb relative to GaSb produces even larger adsorbate bond angles which destabilize the (1×1) structure.

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