

## Atomic geometry and bonding on the GaAs(001)- $\beta 2(2 \times 4)$ surface from *ab initio* pseudopotential calculations

G. P. Srivastava and S. J. Jenkins

*Physics Department, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom*

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We present detailed results of *ab initio* pseudopotential calculations for equilibrium atomic geometry and chemical bonding on the arsenic terminated GaAs(001)- $\beta 2(2 \times 4)$  surface. Of particular note is our finding that there are two distinct Ga-As bond lengths between the first and second layers. This feature is due to the presence of both threefold and fourfold coordinated Ga atoms in the second layer. Our results add significantly to the information available from recent first-principles calculations, and from scanning tunneling microscopy, reflection high-energy electron diffraction, and low-energy electron diffraction analyses.

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The molecular-beam-epitaxy grown GaAs(001) surface is one of the most studied polar semiconductor surfaces, due to its importance for electronic and photonic devices. A whole range of experimental techniques has been employed recently to investigate the atomic and electronic structure of this surface. These include diffraction techniques using low-energy electrons (LEED),<sup>1</sup> high-energy electrons (RHEED),<sup>2</sup> and x rays as well as scanning tunneling microscopy,<sup>3,4</sup> (STM) spectroscopic techniques using Auger electrons and photoemission, and a wide variety of optical probes. On the theoretical side both empirical tight-binding<sup>5</sup> as well as *ab initio* pseudopotential<sup>6-8</sup> methods have been used to study the atomic structure of this surface.

The ideal GaAs(001) surface is terminated with either Ga or As atoms. In experimental growth conditions up to seven different reconstructions of this surface have been reported as a function of stoichiometry (i.e., with different Ga and As compositions).<sup>9,7,10</sup> Previous theoretical and experimental work<sup>8,11,12</sup> suggests that the most likely structure for the As-terminated surface unit cell is characterized by two As dimers and two missing As dimers on the top layer. The second-layer Ga atoms lying beneath the two missing As dimers are also missing, and the exposed third-layer As atoms themselves dimerize. Thus the surface exhibits parallel rows of trenches separated by dimer blocks (i.e., pairs of top-layer As dimers situated on ridges of Ga atoms). In the terminology used by Northrup and Froyen,<sup>8,13</sup> this is referred to as the  $\beta 2(2 \times 4)$  reconstruction and is shown schematically in Fig. 1. To our knowledge, no detailed studies of the atomic geometry and bonding for this reconstruction have been published.

In this work we present the results of first-principles pseudopotential calculations for detailed atomic geometry and bonding on the GaAs(001) $\beta 2(2 \times 4)$  surface. Our results should prove complementary to the first-principles theoretical studies of Northrup and Froyen<sup>8</sup> and experimental studies using LEED (Ref. 1), RHEED (Ref. 2), and STM (Refs. 3 and 4) techniques.

We model the surface reconstruction in the form of a supercell with an artificial periodicity along the surface normal. On the surface the  $2 \times$  periodicity was considered along

$[\bar{1}10]$  and the  $4 \times$  periodicity was considered along  $[110]$ . Along the surface normal the unit cell contained four layers of GaAs (i.e., two layers of Ga and two layers of As) and a vacuum region equivalent to more than six layers of GaAs. The Ga-rich side of the slab was terminated with fictitious hydrogen atoms containing 1.25 electrons each, arranged in a dihydride structure. These fictitious H atoms passivate the back surface *and* help to moderate sloshing of charge backwards and forwards along the supercell, which otherwise would prevent self-consistency for the polar surface considered here.<sup>14</sup> The opposite side of the slab was considered in the  $\beta 2(2 \times 4)$  reconstruction as described above.

The electron-ion interaction was treated by norm-conserving pseudopotentials,<sup>15</sup> and the electron-electron interaction was described within the local density approximation of the density functional theory, including the Ceperley-Alder correlation scheme.<sup>16</sup> The Kohn-Sham equations were solved by diagonalizing the Hamiltonian matrix using an iterative technique.<sup>17</sup> Self-consistency in the electronic degree of freedom was achieved by considering one  $\mathbf{k}$  point at the center of the Brillouin zone. Consideration of additional special  $\mathbf{k}$  points would be unlikely to change our conclusions significantly.<sup>18</sup> Atomic relaxation was achieved by using a conjugate gradient scheme.<sup>17</sup> All the atoms in the supercell were allowed to relax, except for the four fourth-layer Ga atoms lying beneath the dimer block; i.e., those Ga atoms lying beneath the trench *were* allowed to relax. Single-particle wave functions were expanded in a plane-wave basis, with a kinetic energy cutoff of 5 Ry. The theoretical lattice constant for bulk GaAs considered in this work was 5.50 Å. This value was obtained by using the kinetic energy cutoff of 5 Ry, but we do not find that it changes appreciably for higher cutoffs of 8 and 10 Ry. Furthermore, past experience suggests that surface structural parameters in general are also relatively insensitive to the kinetic energy cutoff (see, e.g., Ref. 19).

In discussing our results we will consider the  $x$  axis to be along  $[110]$ , the  $y$  axis to be along  $[\bar{1}10]$ , and the  $z$  axis to be along  $[001]$ . The top view and the  $x$ - $z$  side view of the geometry are shown in Figs. 1(a) and 1(b), respectively. Our

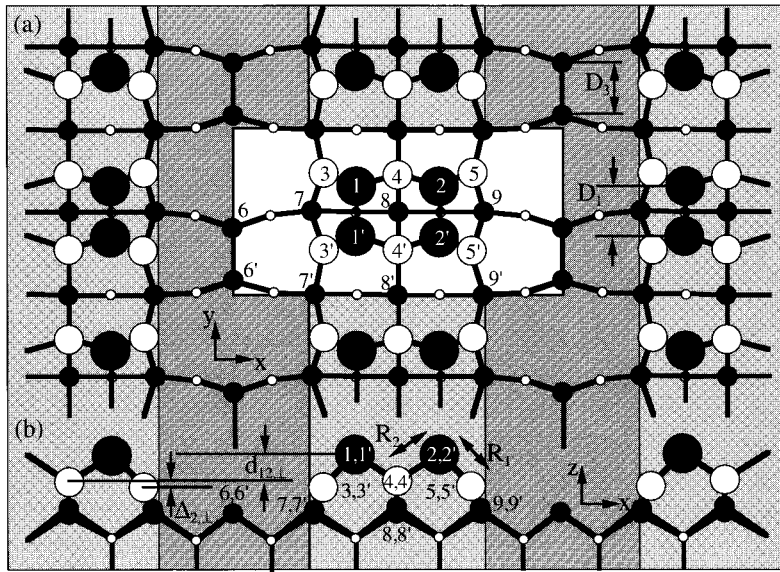


FIG. 1. Relaxed geometry of the GaAs(001)- $\beta 2(2 \times 4)$  surface: (a) top view, and (b) the  $x$ - $z$  side view. Some important geometrical parameters are indicated. The dark and light shaded bands highlight the trenches and the dimer blocks, respectively. The unshaded rectangle indicates the surface unit cell. The filled circles represent As atoms, while the unshaded circles represent Ga atoms. The atom numbers are referred to in the text and the tables.

calculations reveal detailed features of the surface geometry, some of which are shown in Fig. 1 and Tables I and II. In particular we note the following.

*Top layer:* In the top layer (i) the As dimers are symmetric (i.e., show no buckling) with a bond length of 2.39 Å. (ii) Two neighboring As dimers are separated by a distance of 3.94 Å in the  $x$  direction. There is no significant movement of the As dimers in the  $x$  direction. (iii) The width of the trench (i.e., the perpendicular distance between the As dimers on either side of the trench) is 11.62 Å. (iv) Compared to the ideally truncated zinc-blende configuration, the top As layer has relaxed vertically inwards by 0.18 Å with the minimum vertical distance between the top-layer As dimers and the second-layer Ga atoms ( $d_{12,\perp}$ ) being 1.26 Å. This distance possibly can be determined by x-ray standing-wave measurements.

*Second layer:* The Ga atoms in the second layer experience two different types of local bonding configuration. (v)

TABLE I. Displacements of atoms from the ideal zinc-blende positions for the GaAs(001)- $\beta 2(2 \times 4)$  surface. The values given in Å are  $\Delta x$  along [110],  $\Delta y$  along  $[\bar{1}10]$ , and  $\Delta z$  along [001], and correspond to the theoretical lattice constant of 5.50 Å. The displacements of atoms 2, 2', 5, 5', 9 and 9' can be easily worked out by using symmetry present in the unit cell.

Layer	Species	Atom number	$\Delta x$	$\Delta y$	$\Delta z$
1	As	1	-0.03	-0.75	-0.18
		1'	-0.03	0.75	-0.18
2	Ga	3	0.39	-0.10	-0.37
		3'	0.39	0.10	-0.37
		4	0.00	-0.14	-0.07
		4'	0.00	0.14	-0.07
3	As	6	0.00	-0.69	-0.21
		6'	0.00	0.70	-0.18
		7	-0.18	0.00	-0.27
		7'	-0.05	0.00	-0.02
		8	0.00	0.00	-0.23
		8'	0.00	0.00	0.08

The Ga atoms lying along the center line of the dimer block (i.e., atoms labeled 4 and 4' in Fig. 1) are fourfold coordinated and lie relatively close to their ideal zinc-blende sites. To relieve strain, however, these atoms have moved in the  $y$  direction by approximately 0.14 Å to follow the dimerization of the top-layer As atoms, and have also moved vertically downwards by approximately 0.07 Å. (vi) In contrast, the Ga atoms at the edge of the dimer block (atoms 3, 3', 5, 5') are only threefold coordinated (i.e., bonded to only one top layer As) and are pushed significantly inwards towards the center line of the block by 0.39 Å as well as vertically downwards by 0.37 Å also. Thus there is a vertical buckling of  $\Delta_{2,\perp} = 0.30$  Å between the two types of Ga atoms in the second layer. Also, we find that there is a *bimodal* Ga-As bond-length distribution between the top and second layers, being  $R_1 = 2.28$  Å with Ga towards the trench and  $R_2 = 2.42$  Å with Ga in the dimer block. The presence of two types of Ga-As bond lengths possibly can be confirmed by performing a surface extended x-ray absorption fine-structure (SEXAFS) measurement.

*Third layer:* The As atoms in the third layer are in three different configurations. (vii) The exposed third-layer As atoms (atoms 6, 6') form a slightly asymmetric dimer (i.e., show a tilt of  $0.7^\circ$ ) with bond length 2.50 Å and lie at an average height of 0.20 Å below their ideal positions. (viii) The third-layer As atoms within the dimer block can be grouped into those that lie beneath the dimer rows (atoms 7, 8, 9) and those that do not (atoms 7', 8' and 9'). Those

TABLE II. Detailed atomic geometry of the GaAs(001)- $\beta 2(2 \times 4)$  surface calculated from the *ab initio* total-energy pseudopotential calculation with the theoretical lattice constant of 5.50 Å. For the third layer  $\Delta_{3,\perp}^{(1)}$  represents the vertical buckling between atoms 7 and 7', and  $\Delta_{3,\perp}^{(2)}$  represents the vertical buckling between atoms 8 and 8'. (These symbols are not shown in Fig. 1.) The values are in Å.

$D_1$	$D_3$	$d_{12,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}^{(1)}$	$\Delta_{3,\perp}^{(2)}$	$R_1$	$R_2$
2.39	2.50	1.26	0.30	0.25	0.31	2.28	2.42

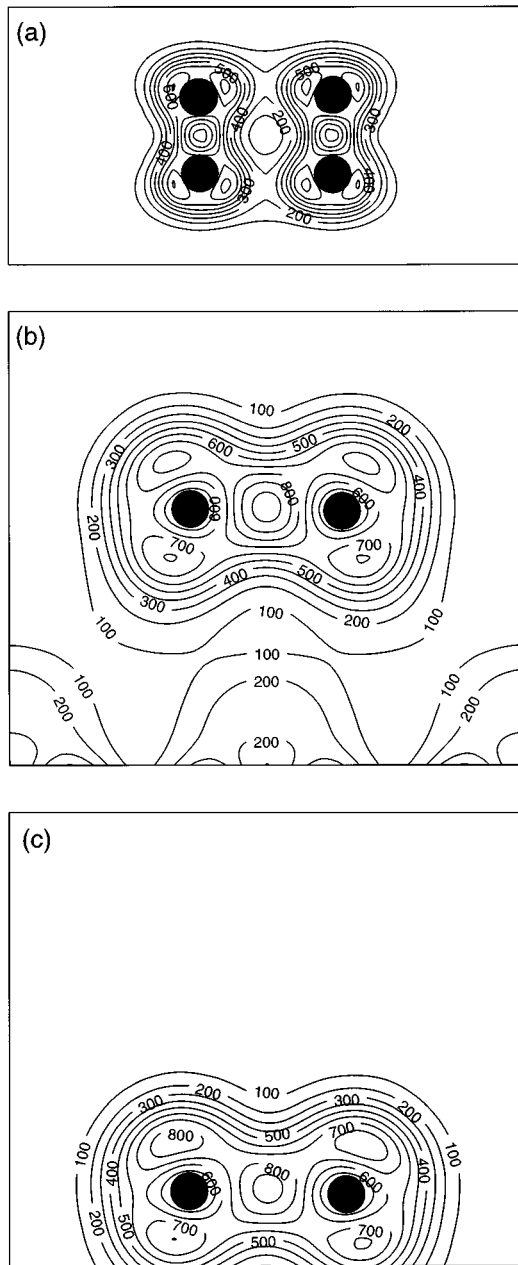


FIG. 2. Total valence charge density plots for the GaAs(001)- $\beta 2(2 \times 4)$  surface: (a) the plot in a horizontal plane covering the surface unit cell and containing two As dimers; (b) the plot in a vertical plane containing a top-layer As dimer; and (c) the plot in a vertical plane through the third-layer As dimer. The charge density  $\rho$  is normalized such that the zero reciprocal lattice vector Fourier component is equal to the number of valence electrons in the supercell, i.e.,  $\rho(\mathbf{G}=0) = 122$ .

that do not lie beneath the dimer rows (atoms 7',8',9') move very little vertically, whereas those that do lie beneath the dimer rows (atoms 7,8,9) move vertically downwards by around 0.25 Å. Thus there is an average vertical buckling ( $\Delta_{3\perp}$ ) of around 0.28 Å between the two types of As atoms in the dimer block third layer. (ix) The only significant movement in the  $x$  direction is for the As atoms under the dimer rows at the edge of the dimer block (atoms 7 and 9). Such atoms move by 0.18 Å away from the center line of the dimer block.

Considering the surface as a whole, the most noticeable feature we observe is the relaxation of the threefold coordinated second-layer Ga atoms (atoms 3,3',5,5') towards the center line of the dimer block as well as downwards into the surface. Such a feature was observed by Ohno<sup>6</sup> for a similar structure [the so-called  $\beta(2 \times 4)$  structure], although we note that our top-layer As dimers move downwards somewhat, whereas his calculations show them moving upwards. The driving force for such a relaxation is the desire for the threefold coordinated Ga atoms to form a trigonal planar geometry, as is observed on III-V(110) surfaces.<sup>18</sup> The difference between the third-layer dimer length ( $D_3$ ) and the first-layer dimer length ( $D_1$ ) can be understood due to the difference in the chemical environments of the As dimer atoms in those layers.

Figure 2 shows the total valence charge density. From Fig. 2(a) it is clear that the top-layer As dimer atoms are covalently bonded, and that there is only a weak electronic communication between the two neighboring dimers in the dimer block. Fig. 2(b) shows the plot in a vertical plane passing through a top-layer As dimer. Once again, the strong covalent nature of the As dimer bonding is seen. There is also evidence of bonding between the top-layer dimer and the second-layer Ga atoms in the dimer block. The maximum of the charge density in both Figs. 2(a) and 2(b) is 1056 in the units explained in the figure caption. In Fig. 2(c) we have plotted the charge density in a vertical plane containing the third-layer As dimers. This is similar to that seen for the first-layer As dimer bond, except that now the maximum of the charge density has reduced to 947. This reduction is consistent with our finding that the third-layer As dimer bond is approximately 4.5% longer than the top-layer As dimer bond.

The different local bonding configurations of the second-

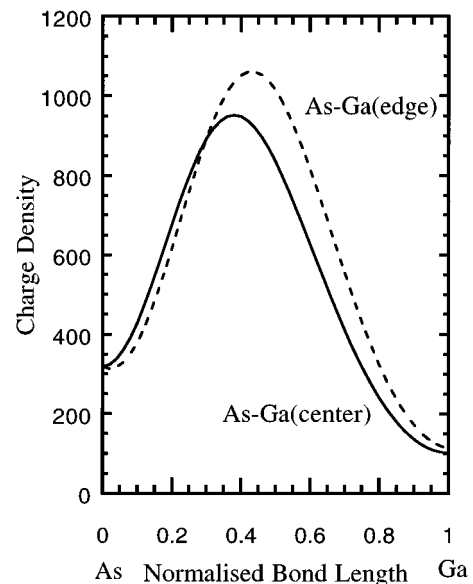


FIG. 3. Total valence charge density along the bond between the top-layer As dimer atom and second-layer Ga atom at the center of the dimer block (solid curve), and the top-layer As dimer atom and the second-layer Ga atom at the edge of the dimer block (dashed curve). The charge density is normalized as explained in the caption to Fig. 2.

layer Ga atoms in the center line of the dimer block (fourfold coordinated atoms 4, 4') and at the edge of the dimer block (threefold coordinated atoms 3,3',5,5') are accompanied by differences in the electronic charge density between the top-layer As atom and the two types of second-layer Ga atoms. As seen in Fig. 3, the charge density between the As atom (e.g., atom 1) and the Ga atom towards the edge of the dimer block (e.g., atom 3) is shifted towards the Ga atom, compared with that between As (e.g., atom 1) and Ga in the center line of the dimer block (e.g., atom 4). Also, the maximum of charge density is greater along As-Ga(edge) (e.g., between atoms 1 and 3) than along As-Ga(center) (e.g., between atoms 1 and 4). Thus the As-Ga(edge) bond is more covalent than the As-Ga(center) bond. This feature can be understood on the basis of simple electron-counting arguments, which indicate that a threefold coordinated Ga atom would tend to possess a slight positive charge with respect to a fourfold coordinated Ga atom, and thus would draw more negative charge from each one of its neighbors.

In summary, we have presented a detailed analysis of *ab initio* pseudopotential results for the atomic geometry and bonding of the  $\beta 2(2 \times 4)$  reconstruction of the GaAs(001)

surface. This structure, originally proposed by Chadi,<sup>5</sup> has only recently been theoretically confirmed by Northrup and Froyen<sup>8</sup> to be the most stable structure for an As coverage of  $\theta=0.75$ , and no previous detailed theoretical or experimental structural parameters have been published. A particularly interesting feature of this surface is found to be a *bimodal* distribution of Ga-As bond lengths between the first and second layers. This is due to the presence of both threefold and fourfold coordinated Ga atoms in the second layer. Our findings regarding charge density and bond lengths should prove complementary to existing theoretical and experimental results, notably from LEED, RHEED, and STM studies. Furthermore, it is hoped that this work will stimulate future experimental work, particularly using x-ray standing wave and SEXAFS techniques, to confirm the structural parameters we have calculated, so that we may gain a better understanding of this fascinating and technologically important surface.

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