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Atomic structures of GaAs(100)-(2 × 4) reconstructions

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Abstract

Atomic structures of the As-rich GaAs(100)-(2 × 4) reconstructions based on converged first-principles total-energy calculations are reported. All geometries are characterized by similar structural elements such as As dimers with a length of about 2.5 Å, dimer vacancies, and a nearly planar configuration of the three-fold coordinated second-layer Ga atoms leading to a steepening of the dimer block. For an As coverage of $\theta=3/4$ we find the two-dimer β_2 phase to be energetically preferred over the three-dimer β phase. A structure with partial replacement of As by Ga in the uppermost layer corresponding to an As coverage of $\theta=\frac{1}{2}$ is found to be slightly less favourable than the α phase of GaAs(100). Geometry parameters are given for all structures and compared with the available experimental results.

Keywords: Density functional calculations; Gallium arsenide; Low index single crystal surfaces; Molecular dynamics; Surface relaxation and reconstruction

The polar GaAs(100) surface has attracted the interest of both experimenters and theoreticians because of its importance for the growth of multi-layer device structures. As-rich (2 × 4)/c(2 × 8) reconstructions, in which the surface is mainly terminated by various arrangements of As dimers, are most important in molecular beam epitaxy (MBE) of GaAs-based layered structures. Three different phases of the (2 × 4) surface have been identified by reflection high-energy electron diffraction (RHEED) experiments [1–3]. The α , β , and γ phases correspond to a characteristic ratio of fractional order intensities. On the basis of a comparison with scanning tunneling microscope (STM) images, Hashizume et al. [2,3] concluded

that all three phases have the same outermost surface layer of the unit cell, which consists of two As dimers and two dimer vacancies. The α phase is assumed to be described by the two-dimer model of Farrel and Palmstrøm [1], with a significant relaxation of the second-layer Ga atoms (cf. Fig. 1). The β phase is proposed to correspond to the two-dimer model originally introduced by Chadi [4] which is characterized by an additional As dimer in the third layer. According to the notation of Northrup and Froyen [5], this structure will be called β_2 in the following (cf. Fig. 1). The γ phase was found to be a mixture of the β phase and the c(4 × 4) phase, with the surface As coverage varying depending on the actual growth conditions. On the other hand, three and two As dimers in the outermost surface layer in (2 × 4) unit cells are seemingly observed by STM [6–8], and are

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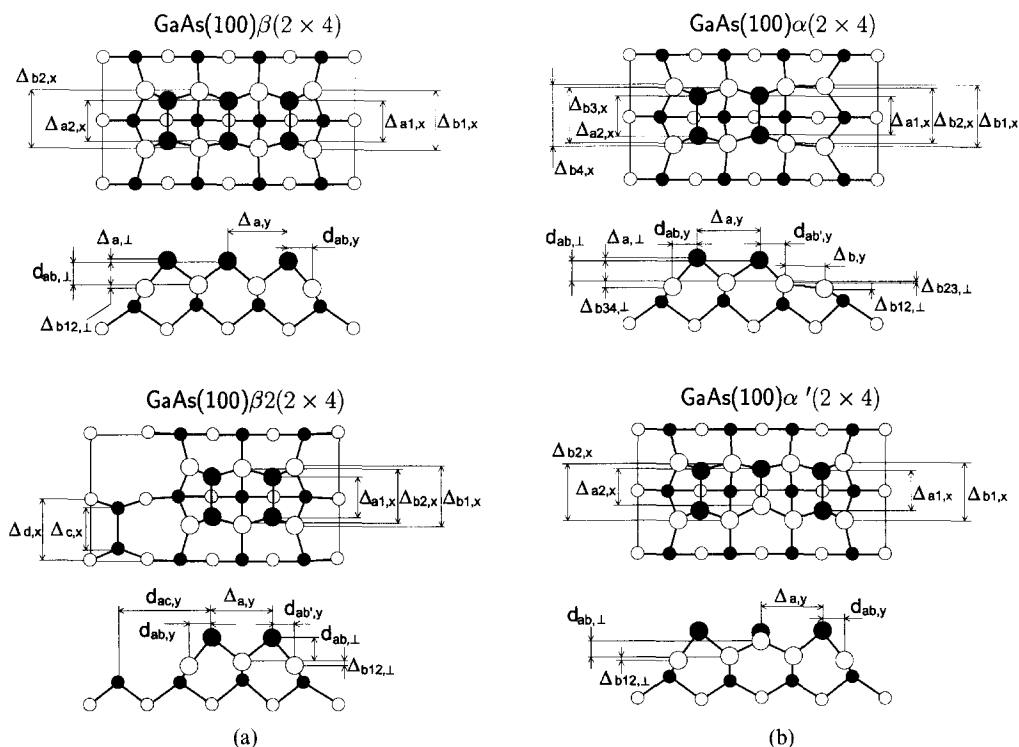


Fig. 1. Top and side view of the relaxed GaAs(100)-(2 × 4) β , $\beta 2$, and α phases. A model for a partial As–Ga replacement in the uppermost layer is denoted by α' . Large (small) filled circles indicate top (third)-layer As atoms, whereas large (small) empty circles represent second (fourth)-layer Ga atoms.

explained by the β and α structure shown in Fig. 1. Both the three-dimer β structure and the two-dimer $\beta 2$ structure correspond to an As coverage of $\theta = 3/4$. Therefore it seems plausible that one of these structures represents the ground-state geometry of the GaAs(100) surface for this particular As coverage. However, *ab initio* calculations by Ohno [9] and Northrup and Froyen [5] came to opposite conclusions concerning the energetic stability. Also, the atomic structure of the α phase, which is stable under less As-rich conditions, is not clear. Northrup and Froyen [5] observe a dimerization of the second-layer Ga atoms, in agreement with the early prediction by Chadi [4] but in contrast to Ohno [9], who rules out a Ga–Ga bonding for the α phase. Also other structural details have been discussed. Recent STM studies [8] indicate an apparent twisting of the As dimers in the α structure. However, symmetric dimers have been found to be in best agreement with X-ray photoelectron

diffraction (XPD) data [10]. A rather wide range of As–As dimer bond lengths can be found in the literature. XPD studies [10] indicate a dimer length of 2.2 Å, energy-dependent photoelectron diffraction (EDPD) experiments [11] determined a value of 2.4 Å, and secondary-ion mass spectrometry (SIMS) investigations [12] found the As dimer atoms to be 2.73 Å apart. An early theoretical study [13] considering As–As dimers in (2 × 1) surface unit cells predicted a dimer length of 2.52 Å. Recent *ab initio* calculations [14] state a value of 2.60 Å. Other structural parameters, such as interplanar distances and relaxations in deeper layers, are even less well known than the precise dimer length and symmetry.

In this Letter we present results of converged first-principles calculations for the atomic structure of the α , β and $\beta 2$ phases of GaAs(100)-(2 × 4). To our knowledge, comprehensive sets of geometrical data are presented for the first time for structures

widely used to explain the As-rich $(2 \times 4)/c(2 \times 8)$ reconstructions. Additionally, we perform calculations on a structure which allows a partial mixing of the substrate constituents in the uppermost layers, as seemingly found in ion-scattering experiments [15].

Our calculations are based on the density functional theory in the local density approximation (DFT-LDA). We consider an artificial periodic slab geometry along the surface normal. The unit cell includes an atomic slab with eight atomic GaAs(100)- (2×4) layers and a vacuum region which is equivalent in thickness. The less interesting Ga-terminated surface of the slab is saturated with fractionally charged ($Z = 1.25$) H atoms [16]. The two bottom layers on this side of the slab are kept frozen, whereas all other atoms are allowed to relax. The electric field resulting from the inequivalence of the two surfaces is accounted for by applying a dipole correction to the electrostatic potential, calculated self-consistently. The electron-ion interaction is simulated by using fully separable, norm-conserving pseudopotentials [17]. For the many-body electron-electron interaction we employ the exchange and correlation potential of Ceperley and Alder [18]. Single-particle orbitals are expanded into plane waves up to an energy cut-off of 15 Ry. k -space integrations are replaced by a sum over a set of special points, corresponding to eight points in the full two-dimensional surface Brillouin zone. The minimum of the total-energy functional [19] with respect to both the electronic and atomic degrees of freedom is found by means of a molecular dynamical approach [20]. The calculations were performed with the theoretical equilibrium lattice constant of 5.56 Å, which is 1.7% smaller than the experimental value. This approach and these numerical parameters have proved successful in determining the structural and dynamical properties of GaAs(110) surfaces precisely [21].

In order to determine the ground-state geometries for the different phases of GaAs(100) considered in this work, we relaxed a series of structures with buckled and twisted dimers. The minimum energy configuration corresponds to symmetric As dimers in the case of α and β structures. For the β_2 phase, we observe a slight dimer buckling of

0.02 Å. The optimized structures for the α , β , and β_2 phases of GaAs(100)- (2×4) are shown in Fig. 1. The corresponding key structural data are compiled in Table 1. From Fig. 1 and Table 1, it is obvious that all these structures have a number of features in common. The dimer length for the topmost As dimers amounts to 2.50 Å for all three structures. The third-layer As dimer occurring for β_2 has a length of 2.52 Å. The dimer lengths are very close to the bond distance of 2.51 Å found for bulk As, where there is three-fold coordination [22]. The three-fold coordinated second-layer Ga atoms bonded to As dimer atoms prefer a nearly planar, sp^2 -like bonding situation. On average they are displaced from their ideal lateral position by about 0.65 Å towards the As dimers. This leads to an upward movement of the As dimers, causing the dimer block to steepen. This relaxation of surface Ga and As atoms is analogous to the buckling of the GaAs(110) surface. As result of the dimer steepening we find the minimum interplanar distance $d_{ab,\perp}$ between the first and second layers to be 1.42 and 1.49 Å (cf. Table 1), which is slightly larger than the ideal bulk spacing of 1.39 Å. The bond length between the three-fold coordinated second-layer Ga atoms and the As dimer atoms is

Table 1
Geometrical parameters (in Å) of the relaxed GaAs(100)- (2×4) β , β_2 , α , and α' structures according to Fig. 1

GaAs(100)- (2×4)	β	β_2	α	α'
$A_{a1,x}$	2.50	2.50	2.50	2.50
$A_{a2,x}$	2.50	—	2.50	2.33
$A_{b1,x}$	3.65	3.65	3.85	3.66
$A_{b2,x}$	3.49	3.52	3.64	3.58
$A_{b3,x}$	—	—	3.50	—
$A_{b4,x}$	—	—	3.66	—
$A_{c,x}$	—	2.52	—	—
$A_{d,x}$	—	3.70	—	—
$A_{a,y}$	3.80	3.82	3.92	3.87
$A_{b,y}$	—	—	2.50	—
$d_{ab,y}$	1.42	1.41	1.50	1.39
$d_{ab',y}$	—	1.44	1.73	—
$d_{ac,y}$	—	5.92	—	—
$A_{a,\perp}$	0.02	—	0.06	—
$A_{b12,\perp}$	0.24	0.28	0.20	0.27
$A_{b23,\perp}$	—	—	0.19	—
$A_{b34,\perp}$	—	—	0.22	—
$d_{ab,\perp}$	1.47	1.49	1.42	0.88

2.32–2.34 Å, somewhat shorter than the ideal bulk bond-length of 2.41 Å. The latter value is, however, essentially preserved in the bonds between the As dimer atoms and the four-fold coordinated cations below. The dimer–dimer distance along the $\times 4$ periodicity amounts to 3.8–3.9 Å, and is thus slightly smaller than the corresponding value at the ideal bulk truncated surface. The further separation of the dimers in the two-dimer α structure compared to the three-dimer block (cf. Table 1) is in agreement with recent STM results [8].

Controversy exists in the theoretical predictions concerning the second-layer atomic structure of the α phase, as discussed above. Our results support the occurrence of a distinct Ga–Ga bond in the second layer with a bond length of 2.51 Å, close to the sum of the Ga covalent radii (2.52 Å, after Ref. [23]). Such a bonding of the originally two-fold coordinated second-layer cations is consistent with electron-counting heuristics [24]. It allows the acceptor-like states to be completely filled, and the donor-like states to be empty.

Another contradiction in the results available so far concerns the energetics of the two β phases. A transformation from the β to the β_2 structure can be achieved by removing two GaAs pairs from each (2×4) unit cell and introducing them into a bulk environment. Therefore, the energy difference between the two structures is independent of the respective value of the chemical potential of Ga and As. Previous work by Ohno [9] indicated that the β_2 structure is higher in energy than the β model by 0.02 eV per (1×1) surface unit-cell. On the other hand, an energetical preference of the $\beta_2(2 \times 4)$ structure by 0.05 eV has been found in Ref. [5]. This contradiction is all the more astonishing as both studies seem to describe essentially the same relaxations. Unfortunately no precise structural data are given in these works. Our own results confirm the finding by Northrup and Froyen [5]. We evaluate the $\beta(2 \times 4)$ structure to be 0.045 eV per (1×1) unit cell higher in energy than the β_2 model. We mention that a slight asymmetry of the $\beta_2(2 \times 4)$ model is energetically more favourable than a complete mirror symmetry perpendicular to the dimer direction. A small shift of the two-dimer block with respect to the third-layer dimer of about 0.07 Å, accompanied by slight

asymmetries in the layers below, lowers the energy considerably (by 0.095 eV). This roughly equals the energy difference between the findings of Ref. [9] and Ref. [5], and may perhaps provide an explanation for their contradicting results. The energetical preference of the two-dimer β_2 structure over the three-dimer β structure seems to contradict STM findings [6–8] with reports of two- and three-dimer structures. A high energy barrier for the transformation of a β into a β_2 structure and the kinetics of the preparation process could be possible explanations for the coexistence of both structures.

As shown in Ref. [5], the higher Madelung energy of the β structure is the decisive factor which makes this structure less stable compared to the β_2 structure. One plausible reason for the energetic difference is the existence of a relatively large negatively charged sub-unit (the three-dimer block) in the (2×4) cell of the β structure. The surface charge is more homogeneously distributed in the case of the β_2 structure. Another possibility for a more favourable charge arrangement is the partial replacement of As by Ga atoms in the outermost layer. Such a mixed composition is not only plausible from theoretical considerations, but is also reported to have been observed in ion scattering experiments [15]. The electron-counting rule does not distinguish between structures in which a three-fold coordinated As atom (with a doubly occupied dangling bond) is replaced by a Ga atom (with an empty dangling bond but two valence electrons less). We have performed calculations for a modified $\beta(2 \times 4)$ structure, where the As–As dimer in the middle of the dimer block has been replaced by an As–Ga pair. The arsenic coverage of such a structure is $\theta = 1/2$, as in the case of the $\alpha(2 \times 4)$ model. We call this structure α' in this work (cf. Fig. 1). The α and α' structures can be compared energetically by using the bulk GaAs bonding energy without taking the chemical potentials of As and Ga into account. The energy for the relaxed α' model is 0.035 eV per (1×1) surface unit-cell higher than for the α structure. The energy difference is comparable to the one found between the β and β_2 structures. It allows us to exclude such a mixing (at least in the particular geometry studied here) from the range of pos-

sible equilibrium structures. However, since the energy difference is not large, such structures may be observed during MBE growth with varying surface concentrations of As and Ga. Therefore, some key geometrical parameters for α' are given in Table 1. Induced by the inequivalence of the central Ga–As bond, a considerable buckling of 0.58 Å in the middle of the dimer block is observed. The two As–As dimers show an opposite buckling of 0.04 Å. The near-planar configuration of the uppermost Ga atom causes an appreciable shortening of the minimum distance between the first and second layers ($d_{ab,\perp} = 0.9$ Å). Apart from this, the geometry of the α' model is rather similar to the three-dimer β structure.

In conclusion, we have studied the atomic structures of the models used to describe the As-rich (2×4) reconstructions of the GaAs(100) surface by means of ab initio calculations. All structural models are characterized by As dimers and structural elements already known from the GaAs(110) surface. Three-fold coordinated nearly planar situated Ga atoms cause the dimer block to steepen. The As–As dimer length is remarkably constant for all models considered, and amounts to 2.5 Å. We find the $\beta 2$ structure to be energetically more favourable than the β structure. A partial mixing of the substrate constituents in the uppermost layer studied for one example gives rise to a metastable structure whose energy is higher than that of the corresponding α phase of the surface.

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