

Surface phase diagram of (2×4) and (4×2) reconstructions of GaAs(001)

W. G. Schmidt* and S. Mirbt

Fysiska Institutionen, Uppsala Universitet, Box 530, 75121 Uppsala, Sweden

F. Bechstedt

IFTO, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany

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Total-energy calculations for a series of (2×4) and (4×2) reconstructed GaAs(001) surfaces not included in previous theoretical studies are presented. A (2×4) surface model containing single anion dimers in the first and third atomic layers is predicted for a balanced surface stoichiometry. It is more stable than the two-As-dimer α structure assumed previously, due to its lower electrostatic energy. Our results for the (4×2) reconstructed surface confirm the two-Ga-dimer $\beta 2$ structure suggested by Biegelsen and co-workers. Nearly degenerate in energy, however, are mixed Ga-As dimers adsorbed on a Ga-terminated substrate.

I. INTRODUCTION

The GaAs(001) surface is known to exhibit a rich variety of ordered phases whose occurrence depends on the preparation conditions (see, e.g., Ref. 1 for a comprehensive review). Among them, the As-rich (2×4) reconstructions were extensively investigated in the past, due to their importance for the molecular beam epitaxial growth of GaAs. Farrell and Palmström² in their reflection high-energy electron diffraction (RHEED) study correlated characteristic patterns with the surface stoichiometry and distinguished among three (2×4) phases, called α , β , and γ . The α phase occurs at the highest substrate temperature and was suggested to correspond to a geometry combining two As dimers in the uppermost atomic layer with Ga-Ga bonds in the layer underneath [Fig. 1(b)]. The β phase, which is stable for more anion-rich conditions, was explained by the three-dimer model due to Chadi.³ Northrup and Froyen⁴ later showed that a somewhat modified structure, called $\beta 2$ [Fig. 1(a)], leads to a lower electrostatic energy and is energetically favored. Other total-energy calculations^{5,6} confirmed this result. The actual occurrence of the $\beta 2(2\times 4)$ structure was proved by *in situ* grazing incidence x-ray diffraction measurements,⁷ dynamical RHEED analysis,⁸ and very recently by highly resolved scanning tunneling microscopy (STM) images.⁹ The γ phase, finally, occurring for even more As-rich surfaces, was found to be a mixture of the β phase and the $c(4\times 4)$ phase, with the surface As coverage varying depending on the actual growth conditions.^{10,11}

The Ga-rich GaAs(001) (4×2) reconstruction has not been studied as extensively. Biegelsen *et al.*¹² interpreted their STM images in terms of the $\beta 2(4\times 2)$ structure [Fig. 1(e)]. This structure has also been supported by Xue *et al.*,¹³ based on STM. No confirmation of that structural model by an independent experimental technique, however, has been obtained. Moreover, Skala and co-workers¹⁴ suggested a radically different model, the (4×2) As-dimer structure [Fig. 1(d)] to explain STM images of the (4×2) reconstructed GaAs surface. A further geometry, shown in Fig. 1(f), which we call $\beta 3(4\times 2)$ in accordance with the generally accepted nomenclature for GaAs(001) surfaces, was sug-

gested by Moriarty *et al.*¹⁵ to account for their STM results. Finally, a three-Ga-dimer model has been concluded from a low-energy electron diffraction analysis¹⁶ of the Ga-rich GaAs(001) (4×2) surface. The three-Ga-dimer model as well as the (4×2) As-dimer structure were found unstable in *ab initio* total-energy calculations, however.^{4,6}

While the GaAs(001) surface structures have long been considered model systems valid also for other III-V(001) surfaces, more recently a series of exceptions were found. For InP and GaP a single-dimer (2×4) structure (“ δ model”) was found to be more stable than the α structure, irrespective of the surface chemical potentials.¹⁷ This structure [Fig. 1(c)], which we call $\alpha 2$ in line with the nomenclature for GaAs, is a very plausible candidate geometry also for GaAs(001) surfaces. Furthermore, general considerations about the stability of III-V surfaces show that under cation-rich conditions the number of anion dangling bonds should be minimized.¹⁸ This condition is clearly not fulfilled in the case of the GaAs(001) $\beta 2(4\times 2)$ surface, while both InP(001) and GaP(001) comply with that rule.^{19–21} Bearing in mind the somewhat contradictory experimental findings for the Ga-rich GaAs(001) (4×2) surface, it thus seems likely that a structure different from the $\beta 2$ may correspond to the actual surface ground state.

Our paper reexamines the phase diagram of GaAs(001) (2×4) and (4×2) surfaces in the light of the recent experimental and theoretical findings for III-V(001) surfaces.

II. METHOD

We use density-functional theory in the local-density approximation together with nonlocal norm-conserving pseudopotentials²² to determine the structurally relaxed ground states of the surface structures. The Ga 3*d* electrons are partially taken into account by means of a nonlocal core correction to the exchange and correlation energy. A massively parallel, real-space finite-difference method²³ is used to deal efficiently with the large unit cells needed to describe the surface. A multigrid technique is employed for convergence acceleration. The spacing of the finest grid used to

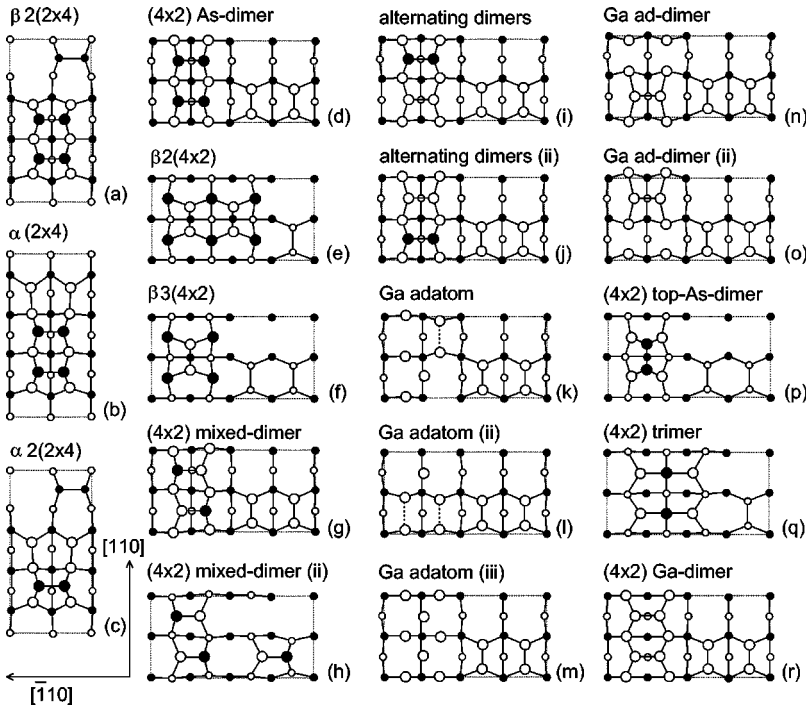


FIG. 1. Top view of relaxed GaAs(001) surface structures, ordered according to the Ga coverage. Empty (filled) circles represent Ga (As) atoms. Positions in the two uppermost atomic layers are indicated by larger symbols.

represent the electronic wave functions and charge density was determined through a series of bulk calculations. We find that structural and electronic properties are converged for a spacing of 0.246 Å. The calculations yield a bulk equilibrium lattice constant of 5.57 Å and a bulk modulus of 0.764 Mbar (experiment²⁴ 5.65 Å and 0.769 Mbar).

To model the surfaces we consider periodic supercells. They contain material slabs about 12 Å thick, separated by 12 Å of vacuum. The surface dangling bonds at the bottom layer are saturated with fractionally charged pseudohydrogen atoms. The geometries investigated were relaxed until all calculated forces were below 20 meV/Å. The atoms in the lowest bilayer were kept frozen in the ideal bulk configuration. Integrations in the surface Brillouin zone were performed using four special \mathbf{k} points in its irreducible part.

In order to compare energetically surface structures representing different stoichiometries one has to take into account the chemical potentials μ of the surface constituents Ga and As. Since the surface is in equilibrium with the bulk material, they are related to each other: their sum equals the chemical potential of bulk GaAs. Consequently, the surface formation energy may be written as a function of a single variable, which we take to be the relative chemical potential of Ga with respect to the bulk Ga phase, $\Delta\mu(\text{Ga})$. The computational accuracy in determining the chemical potentials is of the order of 0.1 eV.²⁵ The uncertainty of the calculated surface energies is less than 0.01 eV per surface atom.

III. RESULTS AND DISCUSSION

The top views of the relaxed surface geometries are shown in Fig. 1. The surface energies of the energetically most favored structures are plotted in Fig. 2.

We probed two (2×4) surface reconstructions for a balanced surface stoichiometry: the two-As-dimer structure known as α geometry and the single-dimer $\alpha 2$ structure favored for InP and GaP(001) surfaces. The $\beta 2(2 \times 4)$ struc-

ture has been calculated for comparison. The surface energy of the $\alpha 2$ structure is 0.034 eV per (1×1) unit cell lower than that of the α model. As both structures have the same stoichiometry there is no dependence on the chemical potentials of the surface constituents. The α structure will be unstable with respect to $\alpha 2$ irrespective of the surface preparation conditions.

That outcome is somewhat surprising, as the α model is seemingly well established.¹ Its geometry has mainly been concluded from filled-state STM images, showing two ‘‘humps’’ along the $[110]$ direction in each unit cell, which were interpreted as As dangling bonds.^{10,11,26} This interpretation is plausible, but not necessarily imperative, as the second-layer Ga-Ga bonds of the $\alpha 2$ model will show up in filled-state STM images close to the positions of the assumed

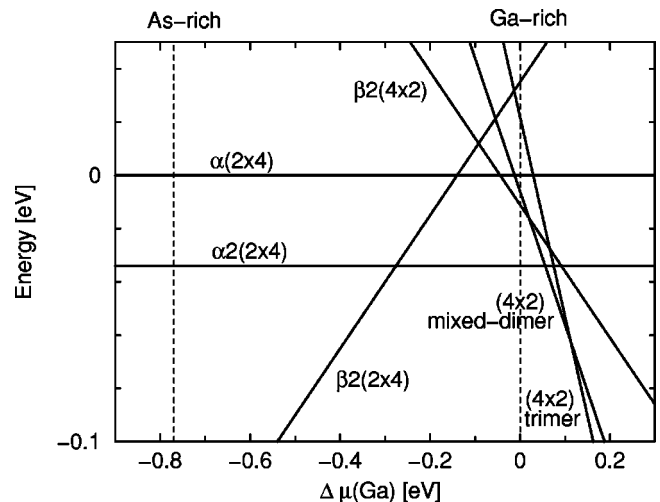


FIG. 2. Relative formation energy per (1×1) unit cell for GaAs surface reconstructions vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu(\text{Ga})$.

TABLE I. Relaxed coordinates (in bohrs, with respect to the theoretical lattice constant) for the uppermost four atomic layers of the GaAs(001) $\alpha 2(2 \times 4)$ surface.

	[110]	$[\bar{1}10]$	[001]
1st layer As dimer	11.95	5.13	8.36
	11.94	9.80	8.34
2nd layer cations	9.00	3.97	5.11
	15.27	3.97	5.28
	19.94	3.78	4.83
	8.97	10.91	5.08
	15.26	10.93	5.25
	19.96	11.12	4.79
3rd layer anions	7.49	0.01	3.25
	14.73	0.01	2.91
	22.15	0.03	3.26
	29.66	1.37	3.33
	7.25	7.42	2.79
	14.94	7.44	2.35
	22.20	7.43	3.17
	29.66	6.09	3.30
4th layer cations	3.36	0.21	0.51
	11.06	14.88	0.28
	18.53	0.01	0.29
	26.19	0.21	0.51
	3.19	7.23	0.32
	11.04	7.45	0.07
	18.75	7.45	0.00
	26.21	7.22	0.49

As atoms. The InP(001) surface provides a recent example of a misinterpretation of cation-cation bonds as anion dangling bonds.^{27,28} Of particular interest in that respect is the observation by Broekman *et al.*²⁶ of a slight asymmetry of the anion dimers of the α phase. The α geometry, possessing mirror symmetry, can hardly explain such a finding. The third-layer As dimer of the $\alpha 2$ structure, however, induces a slight buckling of the upper As dimer of about 0.02 Å (see Table I for geometrical details). The reflectance anisotropy spectrum²⁹ of the α phase of GaAs(001) indicates coexistence of anion dimers oriented along the $[\bar{1}10]$ direction with cation-cation bonds parallel to [110]. These features are present, however, for the $\alpha 2(2 \times 4)$ geometry also: We calculate lengths of 2.47 and 2.50 Å for the uppermost and third-layer As dimers, respectively. The Ga-Ga bond length in the second atomic layer amounts to 2.49 Å. It remains to be seen whether the $\alpha 2$ structure can account for the RHEED spot intensities assigned to the α phase of GaAs(001).^{10,11}

The bonding configuration of the $\alpha 2$ structure is very similar to that of the α model.⁵ Both structures comply with electron-counting heuristics.³⁰ As both geometries have the same number of anion dimers and anion and cation dangling bonds the surface reconstruction parameter²¹ does not discriminate between the two structures energetically. The argument, therefore, that suggests itself to explain the higher stability of the $\alpha 2$ structure is electrostatics. Since the anion dimer bond accommodates six electrons⁵ in addition to the

eight electrons forming the four bonds to the substrate, one expects a Coulomb repulsion between the negatively charged dimers. The surface may lower its electrostatic energy by distributing the dimers more uniformly, as is the case for the $\alpha 2$ structure. In order to estimate the Coulomb contribution to the energy difference between the two geometries we follow a suggestion by Northrup and Froyen:⁴ We assign a charge of $-\frac{1}{2}$ to each of the four As surface atoms, of $\frac{3}{4}$ to threefold-coordinated Ga atoms bonded to As, of $\frac{1}{2}$ to threefold-coordinated Ga atoms bonded to Ga, and finally of $-\frac{1}{4}$ to the remaining second-layer cations. Based on that charge distribution we perform a Madelung summation for a periodic lattice of point charges,

$$S = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|},$$

where the vectors \mathbf{r}_i are the positions of the atoms that have been assigned charge q_i . As expected from the larger dimer-dimer separation for the $\alpha 2$ structure, we find its Madelung energy to be lower. To obtain a quantitative estimate we approximate the screening by simply dividing S by the static dielectric constant of GaAs ($\epsilon \sim 13$). We thus obtain a difference in electrostatic energy between α and $\alpha 2$ of 0.038 eV per (1×1) surface unit cell. That is very close to the energy difference of 0.034 eV obtained from first principles. The quantitative agreement is fortuitous: the concept of homogeneously screened point charges is only a crude approximation. Nevertheless, it shows that the $\alpha 2$ structure is indeed stabilized with respect to α by its more favorable electrostatics. The actual occurrence of the predicted structure, however, remains to be proved experimentally.

Now we turn to the probability of the occurrence of (4×2) structures different from the $\beta 2(4 \times 2)$ model [Fig. 1(e)]. The calculated surface phase diagram (Fig. 2) indicates that (4×2) reconstructions should not form at all, or, considering the limited accuracy of the calculations, should be restricted to extremely Ga-rich surfaces. Similar observations were made in three earlier calculations,^{6,21,25} while Refs. 4 and 31 find the $\beta 2(4 \times 2)$ model to be stable for a slightly larger range of the Ga chemical potential. Those studies, however, did not include the $\alpha 2(2 \times 4)$ structure, which further restricts the allowed energy window for the $\beta 2(4 \times 2)$ geometry. The theoretical results, together with the experiments discussed in the Introduction, thus suggest that the $\beta 2$ structure may not represent the true ground state of the (4×2) reconstructed GaAs surface.

Starting from the knowledge that As dangling bonds are costly in a Ga-rich environment¹⁸ a (4×2) trimer structure [Fig. 1(q)] derived from the $\beta 2$ model was studied. The four surface-exposed second-layer As atoms are removed, the Ga dimers broken, and the cations bonded instead to the third-layer Ga atoms. The energy gain due to the removal of the As dangling bonds is more than counterbalanced, however, by unfavorable bond angles, in particular for the remaining surface anions. The energy difference of 0.032 eV between the $\beta 2$ structure and the trimer model (cf. Table II) excludes the latter.

Moriarty *et al.*¹⁵ proposed a structure that combines a single cation dimer in the first with two Ga dimers in the third atomic layer. This $\beta 3(4 \times 2)$ geometry [Fig. 1(f)] had

TABLE II. Relative formation energy in eV per (1×1) surface unit cell for GaAs surface structures in equilibrium with bulk Ga [$\Delta\mu(\text{Ga})=0$].

Structure	Ga coverage Θ	Energy
$\beta 2(2 \times 4)$	0.250	0.035
$\alpha(2 \times 4)$	0.500	0.000
$\alpha 2(2 \times 4)$	0.500	-0.034
(4×2) As dimer	0.750	0.130
$\beta 2(4 \times 2)$	0.750	-0.011
$\beta 3(4 \times 2)$	0.750	0.072
(4×2) mixed dimer	1.000	-0.006
(4×2) mixed dimer (ii)	1.000	0.008
alternating dimers	1.000	0.130
alternating dimers (ii)	1.000	0.117
Ga adatom	1.125	0.149
Ga adatom (ii)	1.125	0.139
Ga adatom (iii)	1.250	0.085
Ga ad-dimer	1.250	0.071
Ga ad-dimer(ii)	1.250	0.051
(4×2) top-As dimer	1.250	0.148
(4×2) trimer	1.250	0.021
(4×2) Ga dimer	1.500	0.107

already been suggested earlier for InAs(001) (4×2) .³² From both the surface reconstruction parameter²¹ as well as the Madelung energy one would expect the $\beta 3$ and $\beta 2$ geometries to be energetically degenerate. The formation of sp^2 bonded, nearly planar cation dimers leads, however, to an appreciable distortion of the substrate layers.²⁵ The stress can be more easily accommodated in the first compared to the third atomic layer. It is not surprising, therefore, that the $\beta 3(4 \times 2)$ structure is 0.083 eV higher in energy than the $\beta 2$ model. The energy difference gets even larger (cf. Table II) when the second-layer anions are substituted by Ga and the top-dimer atoms are replaced by As [Fig. 1(p)]. The energy gain due to the reduction of anion dangling bonds is counterbalanced by the additional strain.

As we are looking for surface structures in equilibrium with a bulk Ga reservoir, surfaces that do not comply with the electron-counting rule³⁰ or are even metallic were also considered. The considered adatom and ad-dimer geometries are shown in Figs. 1(k)–1(o). All of these structures are energetically unfavorable (cf. Table II), indicating the validity of the electron-counting rule even for extremely Ga-rich surfaces. It is interesting to note that the surface energies of the investigated adatom and ad-dimer structures decrease with increasing Ga coverage. That indicates an attractive interaction of the adsorbed cations toward the formation of Ga clusters.

Based on STM images¹⁴ still another (4×2) geometry [Fig. 1(d)], very different from the $\beta 2$ model, was proposed. The (4×2) As-dimer model has the same (balanced) stoichiometry as the α phase of GaAs. Therefore it is implausible that this structure should be stable for Ga-rich surfaces. Furthermore, the spatial separation between blocks of positively

charged Ga dimers and the negatively charged As-dimer blocks requires an appreciable charge transfer across the surface, which should destabilize this structure. Indeed, we find it to be 0.13 eV higher in energy than the $\alpha(2 \times 4)$ structure. That is in very close agreement with the result of Ref. 4. In order to minimize the lateral charge transfer a replacement of As by Ga dimers is plausible. This substitution also increases the Ga coverage of the surface in agreement with experiment,¹ and reduces the number of anion dangling bonds, costly in Ga-rich conditions.¹⁸ Indeed, we find that the (4×2) Ga-dimer model [Fig. 1(r)] is 0.023 eV lower in energy for Ga-rich conditions. It suffers, however, from compressive stress due to the close proximity of the sp^2 bonded Ga dimers.²⁵ The Ga dimers can be more easily accommodated at the surface if they alternate with As dimers [Figs. 1(i) and 1(j)] or if mixed dimers are formed [Figs. 1(g) and 1(h)]. In particular, the formation of mixed anion-cation dimers on top of a cation-terminated surface turns out to be energetically very favorable. That is in agreement with recent results for cation-rich GaP and InP(001) surfaces.^{19–21} We find the (4×2) mixed-dimer structure [Fig. 1(g)] to be only 0.005 eV higher in energy than the $\beta 2(4 \times 2)$ structure. That energy difference is below the limits of accuracy of the calculations. The existing STM images of Ga-rich GaAs(001) (4×2) surfaces do not, however, bear out the formation of asymmetric Ga-As dimers. The formation of mixed dimers may well be responsible, though, for the observed surface defects at GaAs(001) (4×2) .¹

IV. SUMMARY

We presented results of *ab initio* total-energy calculations for GaAs(001) (2×4) and (4×2) reconstructions. A structural model for the α phase of GaAs(001) (2×4) , characterized by single anion dimers in the first and third atomic layers, is presented. Its higher stability with respect to the two-dimer structure assumed previously for stoichiometric surfaces is related to the more uniformly distributed surface charge. Our results for the Ga-rich GaAs (4×2) reconstructions support the two-dimer $\beta 2$ structure. The formation of mixed Ga-As dimers on top of a Ga-terminated substrate, however, is energetically very close and may account for surface defects.

Note added in proof. Recently, a further, so-called $\zeta(4 \times 2)$ reconstruction model, characterized by two Ga dimers in the second atomic layer and one Ga dimer as well as threefold-coordinated Ga and As atoms in the topmost layer, has been suggested for Ga-rich GaAs(001) surfaces.³³ We probed the total energy of this structure and found it to be 0.093 eV per (1×1) surface unit cell lower than that of the GaAs(001) $\beta 2(4 \times 2)$ surface.

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- *Permanent address: IFTO, FSU, Max-Wien-Platz 1, 07743 Jena, Germany. Email address: W.G.Schmidt@ifto.physik.uni-jena.de
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