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GaAs(0 0 1) surface reconstructions: geometries, chemical bonding and optical properties

W.G. Schmidt^{a,*}, F. Bechstedt^a, J. Bernholc^b^a*Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany*^b*Department of Physics, North Carolina State University, Raleigh, NC 27695-8202, USA*

Abstract

We re-examine the GaAs(0 0 1) surface by means of *first-principles* calculations based on a real-space multigrid method. The $c(4 \times 4)$, (2×4) and (4×2) surface reconstructions minimize the surface energy for anion-rich, stoichiometric and cation-rich surfaces, respectively. Structural models proposed in the literature to explain the Ga-rich GaAs(0 0 1) (4×6) surface are dismissed on energetic grounds. The electronic properties of the novel $\zeta(4 \times 2)$ structure are discussed in detail. We calculate the reflectance anisotropy of the energetically most favoured surfaces. A strong influence of the surface geometry on the optical anisotropy is found. © 2002 Elsevier Science B.V. All rights reserved.

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Until recently, the stoichiometry-dependent surface structure of GaAs(0 0 1) seemed to be well understood [1]. New theoretical [2,3] as well as experimental studies [4,5] show, however, that geometries different from the ones accepted so far occur under certain surface preparation conditions. This concerns in particular the stoichiometric (2×4) reconstructed, the so-called α phase as well as the Ga-rich (4×2) surface.

We investigate the GaAs(0 0 1) surface by *first-principles* density functional (DFT-LDA) calculations using nonlocal pseudopotentials and a real-space multigrid technique [6]. The electronic wave functions are mapped on a grid with a spacing corresponding to 4% of the GaAs bulk lattice constant. Periodic super cells containing 8 (12) atomic (0 0 1) layers and a

vacuum region 8 atomic layers thick are used to calculate the energetic (optical) surface properties. Further, details of the DFT-LDA calculations are like those in Ref. [2].

The calculation of excitation energies within DFT-LDA neglects the quasi-particle character of electrons, leading to a distinct underestimation of excitation energies. In order to calculate optical spectra comparable with experiment, we replace the local exchange and correlation potential used in the DFT-LDA with the nonlocal and energy-dependent self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}'; E)$. In detail, we calculate Σ in the GW approximation, where it is expressed as the product of the single-particle propagator G with the dynamically screened Coulomb interaction W . Since the calculation of optical spectra is computationally expensive, due to the large number of electronic states involved, we use a model dielectric function [7] to calculate W . This approach shifts the E_1 , E'_0 and E_2 critical point (CP) energies from 2.5, 3.9 and 4.1 eV to 3.2, 4.7 and 5.0 eV, respectively. This is in good agreement with

* Corresponding author. Tel.: +49-3641-635910;
fax: +49-3641-635182.
E-mail address: w.g.schmidt@ifo.physik.uni-jena.de
(W.G. Schmidt).

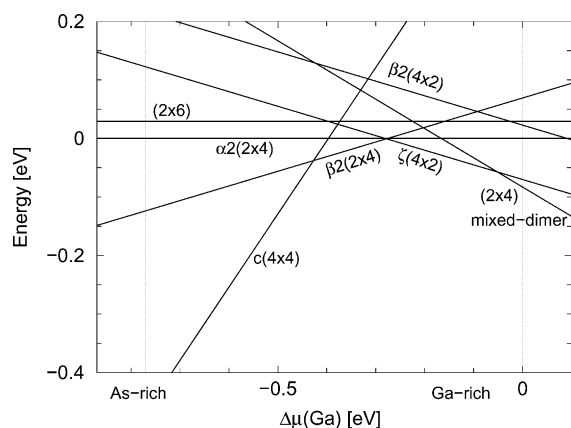


Fig. 1. Relative formation energy per (1×1) unit cell for GaAs surface reconstructions vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu(\text{Ga})$.

the values of 3.1, 4.6 and 5.0 eV measured at low temperatures [8]. The optical spectra presented here are on the same computational footing as our earlier results for InP [9] and GaP(0 0 1) [10] surfaces.

Fig. 1 shows the calculated phase diagram for the energetically relevant surface structures of GaAs(0 0 1). The corresponding geometries are sketched in Fig. 2. For extreme anion-rich surfaces, the formation of three-dimer blocks of As on top of an As-terminated substrate in a $c(4 \times 4)$ symmetry is stable. Moderately As-rich surfaces are characterized by the $\beta_2(2 \times 4)$ structure. As intermediate structures, the $\alpha_2(2 \times 4)$ [2] and—possibly as transient phase—a (2×6) structure may occur. Ga-rich surfaces, finally, form a $\zeta(4 \times 2)$ surface [3]. The calculations predict

for extreme cation-rich surface preparation conditions a (2×4) mixed-dimer structure as observed for InP and GaP surfaces [11]. We are not aware of any experimental evidence supporting this computational finding. Rather the formation of (4×6) symmetries is reported for extreme Ga-rich GaAs surfaces [1]. Xue et al. [1,12] point out that one has to discriminate between a genuine (4×6) reconstruction which is more Ga-rich than the Ga-rich (4×2) reconstruction, and a pseudo- (4×6) phase, which actually consists of a mixture of the (1×6) , the (4×2) and the genuine (4×6) phase. To explain the surface structure of the genuine GaAs(0 0 1) (4×6) surface, Xue et al. [1,12] propose a regular array of Ga clusters consisting of 6–8 atoms on top of a (4×2) -reconstructed GaAs surface (see Fig. 3). The concept of magic numbers of electrons in free metal clusters allows an initial guess on the size of stable Ga clusters. Both experiment and

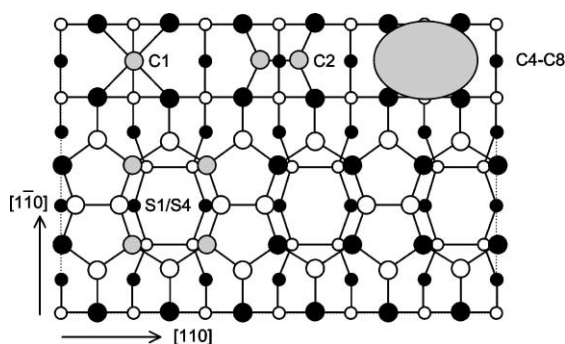


Fig. 3. Top view of the investigated GaAs(0 0 1) (4×6) surface structures described in the text.

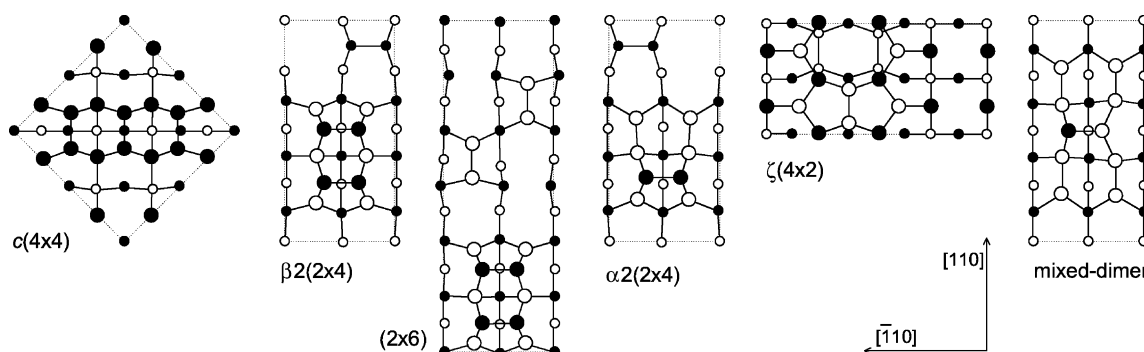


Fig. 2. Top view of relaxed GaAs(0 0 1) surface structures, ordered according to the Ga coverage. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols.

Table 1
Relative surface energies for the (4×6) surface structures described in the text^a

Structure	C1	C2	C4	C5	C6	C8	S1	S4
ΔE (meV)	28	48	119	161	153	225	29	121

^a The energies refer to a (1×1) surface unit cell and are given with respect the Ga-rich GaAs(0 0 1) $\zeta(4 \times 2)$ surface under extreme Ga-rich conditions ($\mu(\text{Ga}) = \mu(\text{Ga})_{\text{bulk}}$).

model calculations indicate that clusters of simple, monovalent metals are particularly stable if they contain a so-called magic number of electrons such as 8, 20, 40, etc. [13,14]. In the present case, of course, the number of electrons in the cluster is modified by the charge transfer from the substrate [15]. If one assumes the cluster to be bonded to four surface anions (as indicated in Fig. 3) which donate the electrons from their occupied dangling bonds into the cluster, a minimum stable metal cluster containing 20 electrons would consist of four Gallium atoms. In this work, a number of adsorbed clusters ranging in size from four to eight atoms (C4, ..., C8) with a variety of shapes and orientations were studied by means of first-principles total energy calculations. The adsorption energies of the most favourable configuration for each cluster size are compiled in Table 1. All investigated cluster geometries are higher in energy than the Ga-rich GaAs(0 0 1) $\zeta(4 \times 2)$ surface, even at the most Ga-rich conditions, where the Ga chemical potential assumes its bulk value. Unless a specific cluster configuration has been missed, the structural model proposed by Xue et al. is thus not borne out by the *ab initio* calculations. Moreover, considering the trend in the surface energies, no indication for the energetic preference of a certain magic cluster size can be recognized. Instead, the larger the clusters get, the more unfavourable their adsorption seems to be.

We also probed the adsorption of single, fourfold-coordinated Ga ad-atoms as suggested by Kumpf et al. [4] (C1) as well as the formation of Ga ad-dimers (C2) as indicated in Fig. 3. However, these ad-structures are only metastable (cf. Table 1). As an alternative geometry, the substitution of one (S1) or four (S4) of the surface anions marked grey in Fig. 3 by Ga atoms was investigated. The substitutional sites are threefold-coordinated and should therefore be favoured by sp^2 -like bonded group-III atoms. Nevertheless, the

two surface structures considered are higher in energy than the GaAs(0 0 1) $\zeta(4 \times 2)$ surface.

Recently, a very different interpretation of what appears to be Ga clusters in the STM images of (4×6) surfaces has been given. Kruse et al. [16] showed that the bright spots disappear upon chemical titration with just 7.5×10^{-4} monolayers of O_2 . The spots do also not show up when empty states are imaged. This led Kruse et al. to conclude that the bright spots arise from surface excess charge localized in the gallium dangling bonds. Repulsion between the trapped negative charge leads to what appears a surface reconstruction. That hypothesis is very interesting but rather speculative. The geometry of the extreme Ga-rich GaAs(0 0 1) surface thus remains an open question.

Detailed accounts of the electronic properties of GaAs surfaces terminated by As or Ga dimers have been published earlier [17,18]. Therefore, we restrict our discussion of the GaAs surface electronic properties to the rather complex $\zeta(4 \times 2)$ surface [3] predicted for Ga-rich surfaces. The surface band structure calculated within DFT-LDA together with the orbital character of the relevant surface states is shown in Fig. 4. The occupied surface states are energetically below the bulk valence band maximum. The bound surface valence bands are derived from surface anion-related orbitals. Interestingly, V1, the highest occupied surface state, is rather delocalized with the probability maximum in the third atomic layer. V2, V3 and V4 are localized at the first-layer anions forming the bridge between first and second atomic layer. These states appear most prominent in filled-state STM images at low bias [3] and were originally interpreted as fingerprints of the second-layer anions of the $\beta 2(4 \times 2)$ surface [19]. The bands derived from unoccupied surface states are pushed above the bulk conduction band minimum. C1 and C3 are derived from empty Ga dimer states in the topmost layer. C2 is an anti-bonding state located between the third-layer anions and the second-layer Ga-dimer atoms. C4 comprises both anion and cation empty dangling bonds in the topmost atomic layer.

In Fig. 5, we show the reflectance anisotropy spectra (RAS) calculated for the energetically favoured surface reconstructions of GaAs. The surface optical anisotropy is strongly related to the surface geometry and therefore well suited to monitor and control the

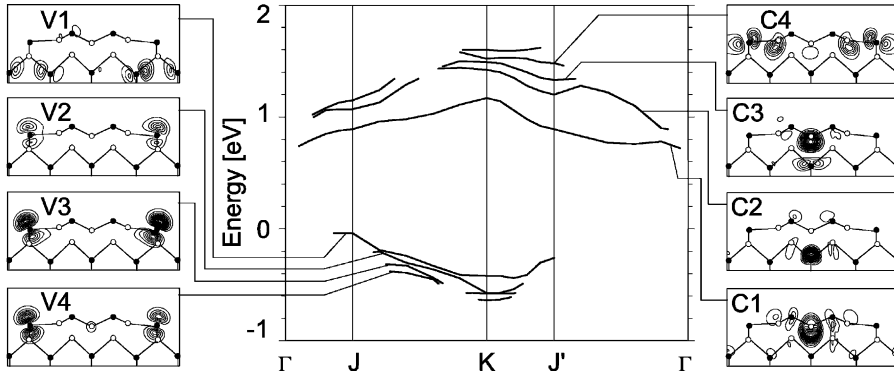


Fig. 4. Surface band structure (bound states) for the GaAs(001) $\zeta(4 \times 2)$ surface. Grey regions indicate the projected bulk band structure. In the left and right panel, the corresponding squared wave functions at K are shown. The contour spacing is $\frac{1}{3} 10^{-3} \text{ Bohr}^{-3}$.

GaAs growth. However, as shown in the middle panel of Fig. 5, not only transitions between surface states contribute to the RAS. The As-rich $c(4 \times 4)$ -reconstructed surface is characterized by positive anisotropies below the E_1 CP energy (S1) and between E_1 and E'_0 (S2), which are mainly caused by As-dimer-related states. The B2 feature at the E_2 CP energy, however,

originates from electronic transitions between surface-modified bulk states. Similar B2 features are present for all surface structures considered. Surface-modified bulk states give also rise to optical anisotropies at the E_1 energy. In particular, for the $\beta 2(2 \times 4)$ structure, a pronounced B1 feature at the E_1 energy appears. In case of the $\alpha 2(2 \times 4)$ and $\zeta(4 \times 2)$ geometries,

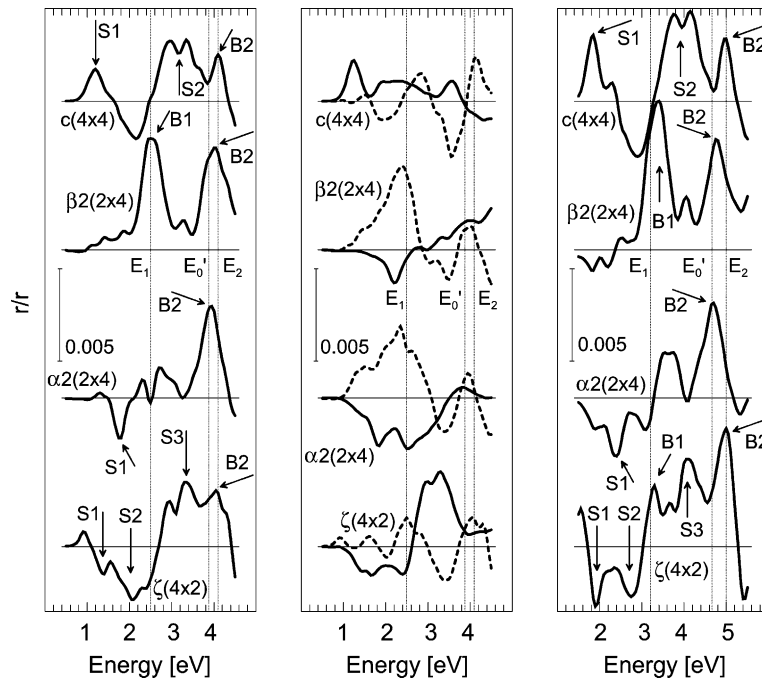


Fig. 5. RAS spectra $[\text{Re}\{(r_{||10} - r_{||10})/(r)\}]$ calculated for GaAs(001). The left panel shows the total signal calculated in DFT-LDA. Solid/dashed lines in the central panel show the contributions of surface/bulk layers to the RAS. In the right panel, GW calculations of the RAS are shown. Dotted lines mark the calculated positions of bulk CP energies.

however, a partial cancellation of optical anisotropies originating from bulk and surface layers occurs at the E_1 energy. Furthermore, characteristic for the $\alpha 2(2 \times 4)$ structure is the negative anisotropy for energies lower than the E_1 transitions. This negative anisotropy is also found for the corresponding structures at InP and GaP(0 0 1) surfaces [9,10] and originates from electronic transitions involving the cation–cation surface bonds. Strong contributions of electronic surface states occur also for the $\zeta(4 \times 2)$ surface. The RAS features S1, S2 and S3 are superpositions of optical anisotropies related to numerous electronic transitions at the surface. No clear-cut assignment to specific surface bonds is possible.

The inclusion of self-energy effects via GW approximation leads to a non-uniform shift of the characteristic peaks to higher energies and changes in the line shape. In particular, the surface-state-related low-energy features for the $\alpha 2$ and ζ structures are strongly affected by the quasi-particle corrections. The RAS spectra calculated in GW approximation are in very good agreement with the experimentally observed trends [20]. A detailed comparison with highly resolved low-temperature data will be published elsewhere.

In summary, we presented first-principles calculations for GaAs(0 0 1) surfaces. An $\alpha 2(2 \times 4)$ surface model containing single anion dimers in the first and third atomic layers is predicted for a balanced surface stoichiometry. Our results for cation-rich $(4 \times 2)/c(8 \times 2)$ -reconstructed surfaces support the newly proposed ζ geometry. The surface electronic structure of the GaAs(0 0 1) $\zeta(4 \times 2)$ surface is dominated by anion dangling bonds energetically close to the bulk valence band maximum, and empty Ga dimer states above the bulk conduction band minimum. A massive parallel implementation of DFT-LDA has enabled us to study for the first time GaAs surface reconstructions as large as (4×6) . Our results seem to exclude the formation of Ga clusters and As–Ga substitution models as possible explanations for the observed (4×6) symmetries on Ga-rich GaAs surfaces. A strong dependence of the surface optical properties on the surface structure is found.

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References

- [1] Q.-K. Xue, T. Hashizume, T. Sakurai, *Prog. Surf. Sci.* 56 (1997) 1.
- [2] W.G. Schmidt, S. Mirbt, F. Bechstedt, *Phys. Rev. B* 62 (2000) 8087.
- [3] S.-H. Lee, W. Moritz, M. Scheffler, *Phys. Rev. Lett.* 85 (2000) 3890.
- [4] C. Kumpf, L.D. Marks, D. Ellis, D. Smilgies, E. Landemark, M. Nielsen, R. Feidenhans'l, J. Zegenhagen, O. Bunk, J.H. Zeysing, Y. Su, R.L. Johnson, *Phys. Rev. Lett.* 86 (2001) 3586.
- [5] D. Paget, Y. Garreau, P. Chiaradia, R. Pinchaux, W.G. Schmidt, *Phys. Rev. B* 64, R161305 (2001).
- [6] E.L. Briggs, D.J. Sullivan, J. Bernholc, *Phys. Rev. B* 54 (1996) 14362.
- [7] F. Bechstedt, R. Del Sole, G. Cappellini, L. Reining, *Solid State Commun.* 84 (1992) 765.
- [8] P. Lautenschlager, M. Garriga, S. Logothetidis, M. Cardona, *Phys. Rev. B* 35 (1987) 9174.
- [9] W.G. Schmidt, N. Esser, A.M. Frisch, P. Vogt, J. Bernholc, F. Bechstedt, M. Zorn, T. Hannappel, S. Visbeck, F. Willig, W. Richter, *Phys. Rev. B* 61 (2000) R16335.
- [10] W.G. Schmidt, J.L. Fattebert, J. Bernholc, F. Bechstedt, *Surf. Rev. Lett.* 6 (1999) 1159.
- [11] W.G. Schmidt, *Appl. Phys. A*, accepted.
- [12] Q.-K. Xue, T. Hashizume, J.M. Zhou, T. Sakata, T. Ohno, T. Sakurai, *Phys. Rev. Lett.* 74 (1995) 3177.
- [13] W.A. de Heer, *Rev. Mod. Phys.* 65 (1993) 611.
- [14] M. Brack, *Rev. Mod. Phys.* 65 (1993) 677.
- [15] S. Tsukamoto, N. Koguchi, *J. Cryst. Growth* 209 (2000) 258.
- [16] P. Kruse, J.G. McLean, A.C. Kummel, *J. Chem. Phys.* 113 (2000) 2060.
- [17] W.G. Schmidt, F. Bechstedt, *Phys. Rev. B* 54 (1996) 16742.
- [18] W.G. Schmidt, *Appl. Phys. A* 65 (1997) 581.
- [19] T. Ohno, *Surf. Sci.* 357/358 (1996) 265.
- [20] A.I. Shkrebtii, N. Esser, W. Richter, W.G. Schmidt, F. Bechstedt, B.O. Fimland, A. Kley, R. Del Sole, *Phys. Rev. Lett.* 81 (1998) 721.