(2×4) and (4×2) reconstructions of GaAs(001): The surface phase diagram re-examined

W.G. Schmidt[1], **S. Mirbt**[2], **F. Bechstedt**[1]

[1] Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität Jena, 07743 Jena, Max-Wien-Platz 1, Germany e-mail: W.G.Schmidt@ifto.physik.uni-jena.de
[2] Fysiska institutionen, Uppsala universitet, Box 530, 75121 Uppsala, Sweden

Abstract Total-energy calculations for a series of (2×4) and (4×2) reconstructed GaAs(001) surfaces not included in previous theoretical studies are presented. Their formation energy is compared with results for seemingly well established (2×4) and (4×2) geometries as well as $c(4\times4)$ and (2×6) reconstructions. A new $\alpha2(2\times4)$ 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. For Ga-rich surfaces the $\zeta(4\times2)$ geometry due to Lee *et al.* is found to be lower in energy than the $\beta2(4\times2)$ surface suggested by Biegelsen and co-workers.

1 Introduction

The GaAs(001) surface exhibits a rich variety of ordered phases whose occurrence depends on the preparation conditions [1]. Farrel and Palmstrøm [2] correlated characteristic RHEED patterns with the surface stoichiometry and distinguished between three (2×4) phases, called α, β and γ. The $\alpha(2\times4)$ and $\beta2(2\times4)$ structures shown in Fig. 1 are generally accepted structural models for the α and β phase [3]. The γ phase occurring for more As-rich surfaces is assumed to be a mixture of the β phase and the $c(4\times4)$ surface, with the surface As coverage varying depending on the growth conditions [4]. The Ga-rich GaAs(001)(4×2) reconstruction is usually explained in the picture of the $\beta2(4\times2)$ structure due to Biegelsen et al. [5].

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 was found to be more stable than the α structure, irrespective of the surface chemical potentials [6]. This structure, which we call $\alpha2$ 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 [7] show that under cation-rich conditions structures other than the GaAs(001)$\beta2(4\times2)$ surface should be energetically favoured.

Our paper re-examines the phase diagram of GaAs(001) by means of *first principles* calculations.

2 Method

We use density-functional theory in the local-density approximation together with *ab initio* pseudopotentials to determine the structurally relaxed ground states of the surface structures. A massively parallel, real-space finite-difference method [8] is used to deal efficiently with the large unit cells. A multigrid technique is employed for convergence acceleration. We model the surfaces by periodic supercells containing 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 pseudohydrogens. Further details can be found in Ref. [9].

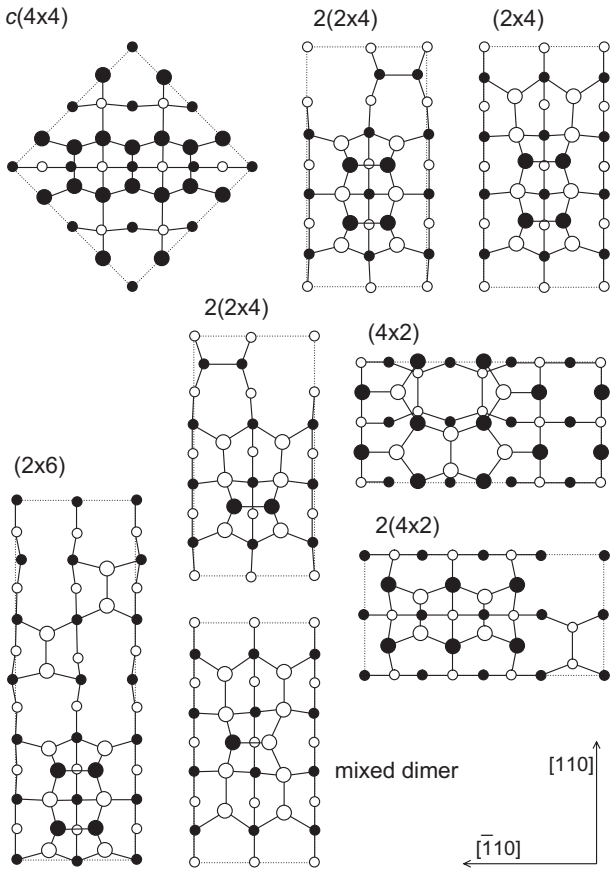

Fig. 1 Top view of relaxed GaAs(001) surface structures. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols.

3 Results and Discussion

We probed a large number of plausible surface geometries for the GaAs(001) surface. In addition to the struc-

tures discussed in detail in Ref. [9] we included the three-As-dimer model for the $c(4\times4)$ reconstructed surface, the (2×6) surface structure proposed in Ref. [5], a modified version of that structure shown in Fig. 1, and the $\zeta(4\times2)$ structure suggested by Lee *et al.* [10]. The surface energies of the energetically favoured structures are plotted in Fig. 2.

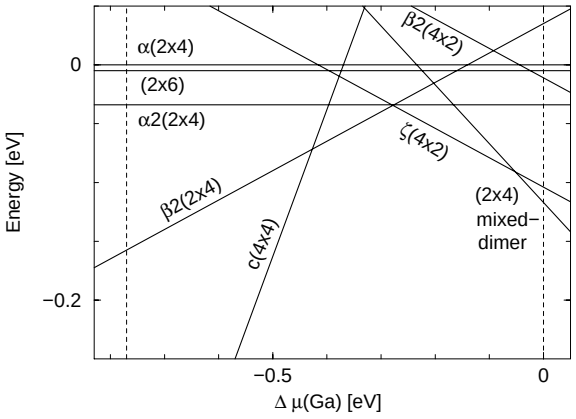

Fig. 2 Relative formation energy per (1×1) unit cell for the GaAs surface reconstructions shown in Fig. 1 vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu$(Ga).

Our results for As-rich surfaces confirm previous findings: the stability of the three-As-dimer $c(4\times4)$ surface for extreme As-rich growth conditions, followed by the $\beta2(2\times4)$ structure for a more moderate As/Ga ratio.

For a balanced surface stoichiometry we consider the two-As-dimer structure known as α geometry, the single-dimer $\alpha2$ structure favoured for InP and GaP(001)(2×4) surfaces and two (2×6) reconstructions. The surface energy of the $\alpha2$ 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 instable with respect to $\alpha2$ irrespective of the surface preparation conditions. That outcome is somewhat surprising, as the α model is seemingly well established [1]. In view of the electrostatic interactions at the surface, however, the lower energy of the $\alpha2$ structure seems plausible: Since the anion dimer bond accommodates 6 electrons [11] in addition to the 8 electrons forming the 4 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 it is the case for the $\alpha2$ structure. In order to estimate the Coulomb contribution to the energy difference between the two geometries we perform a Madelung summation for a periodic lattice of point charges,

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

where the vectors $\mathbf{r}_i$ are the positions of the surface atoms which have been assigned a charge q_i according to the electron counting rule. 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 energies between α and $\alpha2$ of 0.038 eV per (1×1) surface unit cell, very close to the energy difference obtained from *first principles*. The (2×6) structure proposed by Biegelsen and co-workers [5] is 0.006 eV higher in energy than the $\alpha(2\times4)$ surface. The (2×6) structure shown in Fig. 1 is slightly more favoured. It is 0.005 eV lower in energy than the $\alpha(2\times4)$ surface, but still unstable with respect to the $\alpha2$ model.

Our total-energy calculations favour for Ga-rich conditions the $\zeta(4\times2)$ structure proposed by Lee *et al.* over the $\beta2(4\times2)$ model assumed previously. The energy difference of 0.093 eV definitely excludes the occurrence of the $\beta2(4\times2)$ geometry. Again, the energy difference between $\beta2$ and ζ can be traced back to the more favourable electrostatic interaction between the surface atoms of the latter structure [10].

For extreme Ga-rich GaAs(001) surfaces the (2×4) mixed-dimer structure known from InP and GaP surfaces [6] has the lowest energy among the structures considered here. The appearance of (2×4) periodicities, however, is not observed for Ga-rich GaAs surfaces [1]. Either that extreme Ga-rich limit cannot be reached experimentally, or surface structures not included in the present study, such as (4×6) reconstructions, are even lower in energy.

Acknowledgments

We acknowledge financial support by the Göran-Gustafsson foundation and grants of computer time from the John von Neumann-Institut Jülich and the Höchstleistungsrechenzentrum Stuttgart.

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