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

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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(4×4) and (2×6) reconstructions. A new α2(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. For Ga-rich surfaces the ζ(4×2) geometry due to Lee et al. is found to be lower in energy than the β2(4×2) surface suggested by Biegelein 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 α(2×4) and β2(2×4) 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(4×4) 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 β2(4×2) structure due to Biegelein 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 α2 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)β2(4×2) 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 \textit{ab initio} pseudopotentials to

![Fig. 1](image-url)
tures discussed in detail in Ref. [9] we included the three-
As-dimer model for the c(4×4) reconstructed surface, the
(2×6) surface structure proposed in Ref. [5], a modified
version of that structure shown in Fig. 1, and the
(4×2) structure suggested by Lee et al. [10]. The sur-
face 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 αμ(Ga).](image)

Our results for As-rich surfaces confirm previous find-
ings: the stability of the three-As-dimer c(4×4) surface
for extreme As-rich growth conditions, followed by the
β2(2×4) 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 α2 structure favoured for InP and GaP(001) (2×4)
surfaces and two (2×6) reconstructions. The surface en-
ergy of the α2 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 α2 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 α2 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 α2
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,

$$S = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{|r_i - r_j|}$$  \hspace{1cm} (1)

where the vectors $r_i$ 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 ($\varepsilon \sim 13$).
We thus obtain a difference in electrostatic energies be-
tween $\alpha$ and $\alpha_2$ 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
$\alpha$(2×4) surface. The (2×6) structure shown in Fig. 1 is
slightly more favoured. It is 0.005 eV lower in energy
than the $\alpha$(2×4) surface, but still unstable with respect
to the $\alpha_2$ model.

Our total-energy calculations favour for Ga-rich con-
ditions the $\zeta$(4×2) structure proposed by Lee et al. over
the $\beta_2$(4×2) model assumed previously. The energy
difference of 0.093 eV definitely excludes the occurrence
of the $\beta_2$(4×2) geometry. Again, the energy difference
between $\beta_2$ and $\zeta$ 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 sur-
faces [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 ex-
perimentally, or surface structures not included in the
present study, such as (4×6) reconstructions, are even
lower in energy.

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