GaAs and InAs (001) surface structures from large-scale real-space multigrid calculations

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Abstract. There has been a renewed interest in the structure of III-V compound semiconductor (001) surfaces caused by recent experimental and theoretical findings, which indicate that geometries different from the seemingly well-established dimer models describe the surface ground state for specific preparation conditions. We investigate large GaAs and InAs (001) surface reconstructions by means of accurate *first-principles* total-energy calculations based on a real-space multigrid method. The formation of a $\alpha 2(2\times4)$ surface model containing single anion dimers in the first and third atomic atomic layers is predicted for a balanced surface stoichiometry for both GaAs and InAs. This structure is stabilized by its favorable electrostatics. Very complex (4×2) reconstructions consisting of three-fold coordinated surface anions and cations and subsurface dimers describe the surface ground state for cation-rich GaAs and InAs surfaces. The electronic properties of this so-called $\zeta(4\times2)$ structure are discussed in some detail. Several structural models for the Ga-rich GaAs(001)(4×6) surface are investigated, but dismissed on energetic grounds.

1 Introduction

Electronic structure calculations based on density functional theory (DFT) have been enormously successful in predicting and explaining the properties of a wide range of materials. The computational treatment of large and complex structures consisting of hundreds of atoms is still very demanding, though. "Real-space" methods are a very promising technique to reduce the computational cost and thus to enable even larger calculations.

Real-space methods avoid the use of plane waves, which extend throughout the entire system, so that the vast majority of operations are "local". That means on the one hand that parallelization via domain decomposition becomes very effective, since each processor can be assigned a given region of space and only little communication between the processors is needed. On the other hand, advanced mathematical techniques such as the multigrid algorithm can be used to deal efficiently with the various length scales present in the problem. Real-space techniques allow also for a natural implementation of mesh refinement or cluster boundary conditions and seem to be a particularly suitable starting point for the development of $O(N)$ techniques

(N is the number of atoms), which overcome the $O(N^3)$ scaling of traditional electronic structure calculations [1].

We work on an efficient real-space code to calculate surface optical properties highly accurately from *first principles*, i.e., without any empirical or adjustable parameters. The essential building blocks for the code, allowing the calculation of optical properties in independent quasiparticle approximation [2,3] with the inclusion electron-hole interaction effects have been completed [4]. To carry out successfully our project "Simulation of optical spectra for real-time monitoring of semiconductor growth", however, the precise knowlegde of the surface atomic and electronic structure is the necessary prerequisite. This report describes our recent progress in understanding the geometry of the prototypical GaAs and InAs(001) surfaces. The (001) oriented substrates of III-V semiconductors are commonly used in growth technologies like molecular beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOVPE). The growth of GaAs and InAs is routinely monitored by means of optical spectroscopy. Nevertheless, the observed spectral features are only poorly understood. This makes them ideal candidates for our study.

2 Method

Density-functional theory in the local-density approximation (DFT-LDA) together with nonlocal norm-conserving pseudopotentials [5] is used to determine the structurally relaxed ground states of the surface structures. The Ga $3d$ and In $4d$ electrons, respectively, 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 method [6] is used to deal efficiently with the large unit cells needed to describe the surface. Thereby a real-space mesh is used to represent the wavefunctions, the charge density, and the ionic pseudopotentials. The density functional equations are discretized using a generalized eigenvalue form:

$$H_{mehr}[\psi_n] = \frac{1}{2} A_{mehr}[\psi_n] + B_{mehr}[V_{eff}\psi_n] = \epsilon_n B_{mehr}[\psi_n] \ ,$$

where A_{mehr} and B_{mehr} are the components of the *Mehrstellen* discretization, which is based on Hermite's generalization of Taylor's theorem. It uses a weighted sum of the wavefunction and potential values to improve the accuracy of the discretization of the entire differential equation. Only nearest and next-nearest neighbour points are used in the discretization. This short-ranged representation of the equation leads to an efficient domain-decomposition-based implementation on massively parallel computers (for details see Ref. [6]). The efficiency of the massively parallel implementation is illustrated in Fig. 1, which shows the speedup in execution time for a given problem as the number of PE's is increased. Typical jobs utilize 32 to 256 PE's and run from 2 to 12 hours. To efficiently solve the discretized equations, we use multigrid iteration techniques that accelerate convergence by

employing a sequence of grids of varying resolutions. The solution is obtained on a grid fine enough to accurately represent the pseudopotentials and the electronic wavefunctions. We find that the structural and electronic properties of GaAs and InAs are converged for a spacing corresponding to 4% of the respective bulk lattice constants. However, the iterations are accelerated by solving both the Poisson and the density functional equations on coarser grids and transferring the resulting corrections to the fine grid. This procedure provides excellent preconditioning for all length scales present in our systems and leads to very fast convergence rates. The operation count to converge one wave function with a fixed potential is $O(N_{grid})$.

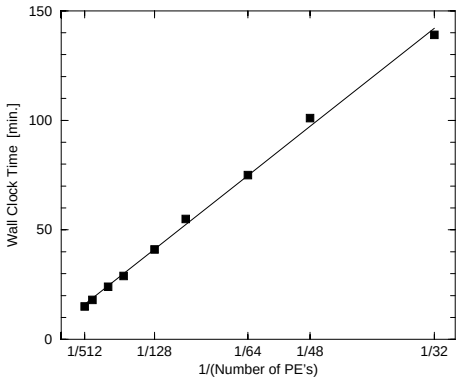

Fig. 1. Execution time needed to determine the structurally relaxed ground state of the GaAs(001)$c(4\times4)$ surface on the Cray-T3E of the Höchstleistungsrechenzentrum in Stuttgart is plotted vs number of processors. The surface is modeled by a super cell containing 70 atoms. The solid line is a guide to the eye.

The surfaces are modeled by using periodic supercells. They contain material slabs consisting of 60 to 270 atoms which are about 12 Å thick, separated by 12 Å of vacuum. The surface dangling bonds at the bottom layer are saturated with fractionally charged pseudohydrogens. We relax the investigated geometries until all calculated forces are below 20 meV/Å. The atoms in the lowest bilayer remain in the their ideal bulk configuration. Integrations in the surface Brillouin zone are performed over four special **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. Since the surface is in equilibrium with the bulk material, they are related to each other: their sum equals the chemical potential of the bulk semiconductor. 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 the cation with respect to its bulk phase, $\Delta\mu$(Ga,In). The computational accuracy in determining the chemical potentials is of the order of 0.1 eV. The uncertainty of the calculated surface energies is less than 0.01 eV per surface atom.

3 Results and Discussion

3.1 GaAs

The GaAs(001) surface is known to exhibit a very rich variety of ordered phases whose occurrence depends on the preparation conditions (see, e.g., Ref. [7]). Among them, the As-rich (2×4) reconstructions were extensively investigated in the past, due to their importance for the MBE growth of GaAs. Three different (2×4) surfaces phases, called α, β and γ, are known.

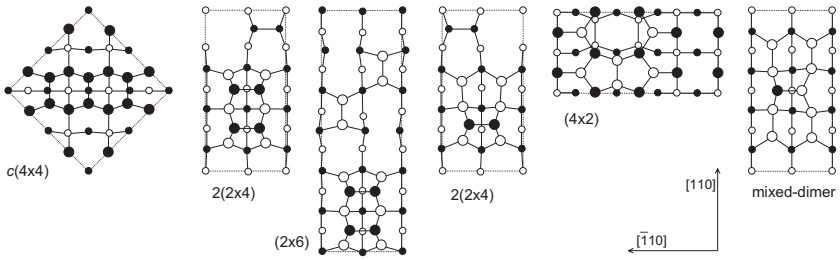

Fig. 2. Top view of relaxed GaAs(001) surface structures, ordered according to the Ga coverage. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols.

The α phase occurs at the highest substrate temperature and is commomly assumed to correspond to a geometry combining two As dimers in the uppermost atomic layer with Ga-Ga bonds in the layer underneath. The same stoichiometry, however, can be realized with a slightly modified geometry, called $\alpha 2(2\times4)$, as shown in Fig. 2 [8]. We find this structure to be 0.034 eV per (1×1) unit cell lower in energy than 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 $\alpha 2$ irrespective of the surface preparation conditions. That result is somewhat surprising, as the α model is seemingly well established [7]. The reflectance anisotropy spectrum of the α phase of GaAs(001) [9] indicates a co-existence of anion dimers oriented along the [$\bar{1}$10] direction with cation-cation bonds parallel to [110]. These features are present, however, also for the $\alpha 2(2\times4)$ geometry. It still remains to be seen whether the $\alpha 2$ structure can account for the RHEED spot intensities assigned to the α phase of GaAs(001).

The bonding configuration of the $\alpha 2$ structure is very similar to the one of the α model. In order to understand its higher stability we analyzed the electrostatic interactions at the surface. Point charges were assigned to the surface atoms according to the *electron counting rule*, i.e., all acceptor-like states such as anion dangling bonds are filled, wheras cation dangling bonds are empty.

Based on such a charge distribution one can then 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 which have been assigned charge q_i. The screening can be approximated by dividing S by the static dielectric constant of GaAs ($\epsilon \sim 13$). That rough estimate yields a difference in electrostatic energies between α and $\alpha 2$ of 0.038 eV per (1×1) surface unit cell. That is remarkably close to the energy difference of 0.034 eV obtained from *first principles*. The good agreement indicates that the $\alpha 2$ structure is indeed stabilized with respect to α by its more favourable electrostatics. The actual occurrence of the predicted structure, however, remains to be proven experimentally. Our results for the geometry of the more As-rich GaAs(001)$\beta 2$(2×4) and c(4×4) reconstructions (see. Fig. 2) agree with earlier findings.

The atomic structure of the Ga-rich GaAs(001)(4×2) reconstruction has been puzzling surface scientists for several years (see, e.g., Ref. [10]). Very recently a rather complex surface geometry, a so-called ζ structure (cf. Fig. 2) has been proposed on the basis of total-energy calculations [11]. The stability of the ζ structure with respect to all previously suggested (4×2) geometries was confirmed by two of the present authors in Refs. [8,12]. The calculated band structure of the ζ(4×2) surface together with the orbital character of the relevant surface states is shown in Fig. 3. The occupied surface states

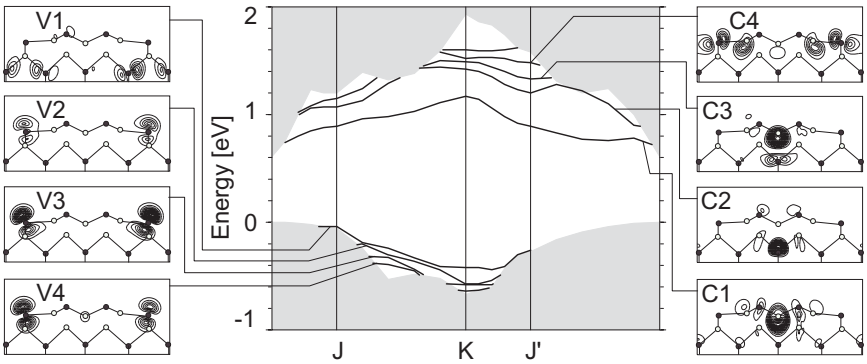

Fig. 3. Surface band structure (bound states) for the GaAs(001)ζ(4×2) surface. Gray regions indicate the projected bulk band structure. In the left and right panel, the corresponding squared wave functions at K are shown. The contour spacing is $\frac{1}{3}10^{-3}$ Bohr $^{-3}$.

are energetically below the bulk valence band maximum. The bound surface

valence bands are derived from surface anion related orbitals. Interestingly, $V1$, the highest 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 [11] and were originally interpreted as fingerprints of the second-layer anions of the $\beta 2(4\times2)$ surface [13]. 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 antibonding 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.

When discussing the band structure in Fig. 3, a word of caution is in order. The presented band structure suffers from the well-known DFT-LDA gap problem, i.e., the underestimation of the excitation energies. The inclusion of electronic self-energy effects may lead to different energy shifts for bulk and surface state energies, as we have demonstrated for GaP(001) and InP(001) surfaces [14,15]. Experience shows, however, that the relative ordering and orbital character of the surface states are usually reliably described within DFT-LDA.

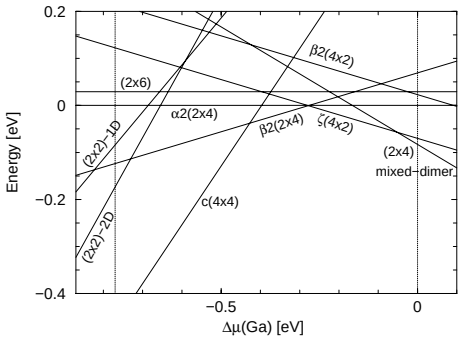

Fig. 4. Relative formation energy per (1×1) unit cell for GaAs surface reconstructions vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu$(Ga).

Structural models were also proposed for GaAs(001) surface reconstructions larger than (2×4) or (4×2). A (1×6) symmetry was observed by electron diffraction [7] as a non-equilibrium or transient phase between As and Ga-rich surfaces. STM images by Biegelsen and co-workers [16] and Kuball *et al.* [17] revealed that (2×6) and (6×6) reconstructed domains are responsible for the observed LEED patterns. The energy of Biegelsen's model for the (2×6) surface has been approximated by a linear combination of structural motifs (LCSM) method by Zhang and Zunger [18]. They found it to be higher in energy than the $\alpha(2\times4)$ structure by 0.034 eV per (1×1) surface unit cell. More precise *ab initio* calculations [12] indicate that the energy differences is actually much smaller, 0.006 eV. By a simple rearrangement of the As dimers in blocks instead of zig-zag

chains, resulting in the (2×6) structure shown in Fig. 2, a further lowering of the surface energy below the value of the $\alpha(2\times4)$ structure is possible [12]. Still, the energy gain is not sufficient to make this (2×6) geometry more favourable than the newly proposed $\alpha2(2\times4)$ structure (see calculated phase diagram in Fig. 4). The surface energy of the (6×6) model suggested in Ref. [17] will very likely be in the same range as the one calculated for the (2×6) reconstruction, as both models are rather similar. The stability of the stoichiometric $\alpha2(2\times4)$ surface is limited to a very small window of preparation conditions as can be seen from Fig. 4. Given the higher energy of the (2×6) and probably also the (6×6) surface, these structures are only metastable. This may explain their low longe-range order.

The calculated phase diagram for GaAs(001) in Fig. 4 indicates that for extreme Ga-rich conditions the $\zeta(4\times2)$ surface should transform into a (2×4) reconstructed mixed-dimer structure. Such a phase transition is not observed experimentally. Rather a (4×6) surface forms. The atomic structure of this GaAs(001)(4×6) surface is extensively discussed in the literature (see Ref. [7] for a comprehensive review). Xue *et al.* 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(001)(4×6) surface Xue *et al.* [7,10] propose a regular array of Ga clusters containing 6 to 8 atoms on top of a (4×2) reconstructed GaAs surface (see Fig. 5).

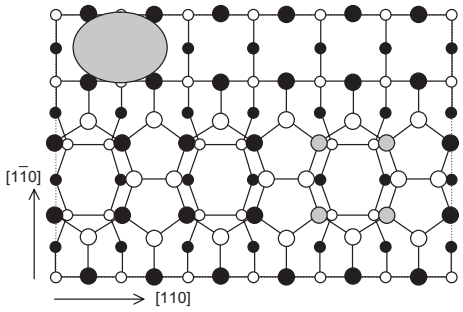

Fig. 5. Top view of investigated GaAs(001)(4×6) surface. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols. The large oval shape indicates trial Ga clusters. Positions of surface anions which were substituted by Ga in the substitution models are filled gray.

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 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,.. [19]. In the present case, of course, the number of electrons in the cluster is modified by the charge transfer from the substrate. If one assumes the cluster to be bonded to four surface anions as indicated in Fig. 5, each anion donating the electrons from its doubly occupied dangling bond into the cluster, a minimum stable metal

cluster containing 20 electrons would consist of four Gallium atoms. In the present 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 Tab. 1. All investigated cluster geometries are higher in energy than the Ga-rich GaAs(001)$\zeta(4\times2)$ 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.

As an alternative geometry the substitution of one (S1) or four (S4) of the surface anions marked gray in Fig. 5 by Ga atoms was investigated. The substitutional sites are three-fold 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(001)$\zeta(4\times2)$ surface.

structure	C4	C5	C6	C8	S1	S4
energy in meV	119	161	153	225	29	121

Table 1. Relative surface energies for adsorbed Ga cluster configurations (C4...C8) as well as for substitutional models (S1 and S4). The energies refer to a (1×1) surface unit cell and are given with respect the Ga-rich GaAs(001)$\zeta(4\times2)$ surface under extreme Ga-rich conditions ($\mu(\mathrm{Ga}) = \mu(\mathrm{Ga})_{bulk}$).

Recently, a very different interpretation of what appears to be Ga clusters in the STM images of (4×6) surfaces has been given. Kruse and co-workers [20] showed that the bright spots disappear upon chemical titration with just $7.5 \cdot 10^{-4}$ 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 (4×6) reconstructed GaAs(001) surface thus remains an open question.

3.2 InAs

The surface phase diagram of InAs(001), while less investigated, appears to be similar to the one of GaAs. (4×2), (2×4) and $c(4\times4)$ reconstructions are observed with increasing surface As content. STM images of (2×4) reconstructed InAs surfaces are interpreted in terms of the $\beta2(2\times4)$ geometry (cf. Fig. 2) for the more As-rich case, while a $\alpha2(2\times4)$ structure seems to form after annealing. This picture is supported by *first-principles* total-energy calculations [21,22].

Less clear is the structure of the In-rich (4×2) surface. A $\beta 3(4\times2)$ geometry was proposed on the basis of STM images [23], while total-energy calculations by Ratsch *et al.* [21] failed to find a stable (4×2) surface. In the present study the $\zeta(4\times2)$ structure suggested by Lee *et al.* [11] for Ga-rich GaAs surfaces was probed for InAs(001). It turns indeed out to be energetically stable for a certain window of In-rich surface preparation conditions as shown in the calculated phase diagram in Fig. 6. Also a very recent X-ray diffraction analysis of $c(8\times2)$ reconstructed InAs(001) indicates a ζ-like geometry [24]. Therefore it seems that the ζ structure solves the structural puzzle of the In-rich InAs(001)(4×2) surface.

For extreme In-rich conditions the calculations predict a change of reconstruction again. A (2×4) mixed-dimer structure should then be favoured. Such a second phase transition is not observed experimentally. The theoretical finding may well be an artefact of the limited accuracy in the calculation of the surface phase diagram, in particular with respect to the boundaries of the thermodynamically allowed region. Also the occurrence of a modified, even more In-rich $\zeta(4\times2)$ structure, for example the adsorption of additional cations as suggested in Ref. [24], would explain the apparent contradiction.

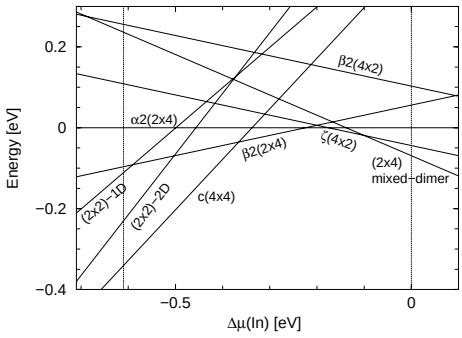

Fig. 6. Relative formation energy per (1×1) unit cell for InAs surface reconstructions vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu$(In).

For As-rich surfaces, finally, the three-dimer $c(4\times4)$ structure known from GaAs has the lowest energy.

4 Summary

We presented *first-principles* total-energy calculations on the structure and stability of (001) surfaces of GaAs and InAs. A $\alpha 2(2\times4)$ surface model containing single anion dimers in the first and third atomic atomic layers is predicted for a balanced surface stoichiometry. Our results for cation-rich $(4\times2)/c(8\times2)$ reconstructed surfaces support the newly proposed ζ geometry. The surface electronic structure of the GaAs(001)$\zeta(4\times2)$ 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 massively 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 explanation for the observed (4×6) symmetries on Ga-rich GaAs surfaces.

Grants of computer time from the Höchstleistungsrechenzentrum Stuttgart, the Leibniz-Rechenzentrum München and the John von Neumann-Institut Jülich are gratefully acknowledged.

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