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In-induced (4 × 2) reconstructions of GaAs(001) surfaces

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Abstract

We present *first-principles* total-energy calculations on In-terminated GaAs(001)(2 × 4) surfaces. The atomic structures and energetics of two structural models suggested from recent experiments are discussed. We favour a surface structure similar to the GaAs(001)β2(4 × 2) surface, where all Ga dimers are replaced by indium. Its stability, however, is limited to In- and As-rich conditions. The surface electronic structure is characterized by filled In sp^2-like states energetically close to the bulk valence band edge and empty π-bonding and π^*-antibonding combinations of In p_z orbitals in the upper half of the GaAs bulk band gap. © 1998 Elsevier Science B.V.

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1. Introduction

The GaAs(001) surface is one of the most studied polar semiconductor surfaces, because of its importance for electronic and photonic devices. A number of experimental and theoretical studies have addressed the structural, energetical and electronic properties of the different reconstructions of the clean surface [1–5]. Much less is known about the modification of the surface properties through deposition of other species.

The growth of indium on GaAs(001) surfaces has recently been subject to scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and optical spectroscopy [6,7]. After deposition of indium amounts between 0.2 and 1.6 monolayers followed by annealing, both As- and Ga-terminated surfaces show a clear c(8 × 2) LEED pattern. Interestingly, the surface roughness of these In-terminated surfaces is strongly reduced, which has been explained [7] by the larger mobility of the In surface atoms [8]. Mainly on grounds of STM images and reflectance anisotropy spectra (RAS) Resch-Esser et al. [7] propose an In-dimer based surface structure similar to the one which is assumed to describe the ground state of the Ga-rich GaAs(001)(4 × 2)/c(8 × 2) surface [1,9]. Thereby the uppermost two Ga dimers are replaced by In. In accordance with the notation of Northrup and Froyen [1] we denote the proposed model as In/GaAs(001)$\beta 2_2$ (cf. Fig. 1).

In our study we apply converged ab initio total-energy calculations to investigate the atomic structure and energetical properties of the In/GaAs(001)(4 × 2) interface. In addition to the In/GaAs(001)$\beta 2_2$ structure suggested by Resch-

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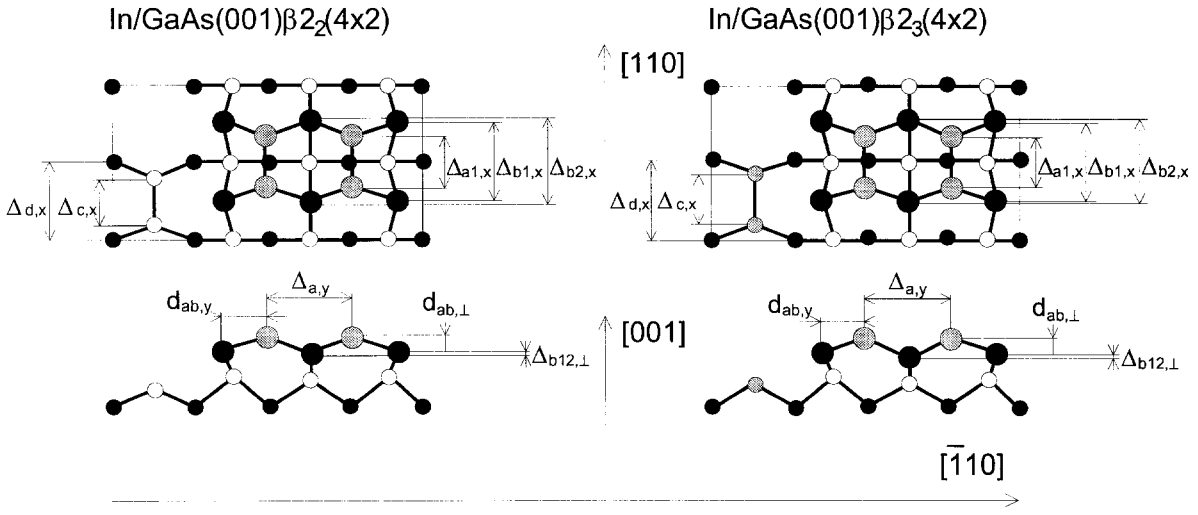

Fig. 1. Top and side view of relaxed In/GaAs(001)(4 × 2) structures. Large (small) circles indicate top and second (third and fourth) layer atoms. Substrate anions (substrate cations, indium atoms) are denoted by full (empty, shaded) symbols.

Esser et al. [7] we also investigate a surface structure, where all three Ga dimers are replaced by In, denoted as $\beta 2_3$, cf. Fig. 1.

2. Method

We apply density-functional theory in local-density approximation (DFT-LDA). The surface is simulated by a periodic slab with 7 atomic (001) layers and a vacuum region equivalent in thickness. The Ga-terminated bottom of the slab is saturated with fractionally ($Z = 1.25$) charged H atoms. The two bottom layers on this side of the slab are kept frozen, whereas all other atoms are relaxed using a molecular-dynamical approach [10]. The electric field resulting from the inequivalence of the two surfaces is accounted for by applying a dipole correction to the electrostatic potential calculated self-consistently. Single-particle orbitals are expanded into plane waves up to an energy cut-off of 15 Ry. $\boldsymbol{k}$-space integrations are replaced by a sum over four special points in the irreducible part of the surface Brillouin zone.

Our calculations are on the same footing as recent studies on As-rich GaAs(001)(2 × 4) [3,5] and Ga-rich GaAs(001)(4 × 2) [9] reconstructions. This allows precise comparisons and the determination of the chemical trend.

3. Results

3.1. Atomic structure

To determine the ground state geometries for the adsorption models $\beta 2_2$ and $\beta 2_3$ (Fig. 1) we relaxed a series of structures with buckled and twisted dimers until the forces acting on the atoms were below 0.025 eV Å^{-1}. We observe a very slight buckling of less than 0.02 Å, accompanied by a nearly vanishing twisting of the cation dimers. Both structures are characterized by In-dimer lengths of 2.63–2.65 Å, about 8% smaller than the sum of the In covalent radii [11]. This bond contraction can be explained by the tendency of the three-fold coordinated In atoms to assume a planar, sp^2-like bonding situation, which leads to compressive stress in the second atomic layer: The three-fold coordinated surface anions are laterally pushed away from their ideal positions by about 0.5 Å. Further structural details are given in Table 1. The interface geometries are very similar to

Table 1
Geometrical parameters in of two models for relaxed In/GaAs(001)(4 × 2) structures according to Fig. 1. For comparison structural data for the Ga-rich GaAs(001)$\beta 2(4\times 2)$ (Ref. [9]) are also given

	$\Delta_{a1,}$	$\Delta_{b1,x}$	$\Delta_{b2,x}$	$\Delta_{c,x}$	$\Delta_{d,x}$	$\Delta_{a,y}$	$d_{ab,y}$	$\Delta_{b12,\perp}$	$d_{ab,\perp}$
In/GaAs(001)$\beta 2_2(4\times 2)$	2.64	4.08	4.18	2.39	3.87	4.39	2.22	0.16	0.75
In/GaAs(001)$\beta 2_3(4\times 2)$	2.65	4.07	4.17	2.63	3.84	4.44	2.23	0.13	0.76
GaAs(001)$\beta 2(4\times 2)$	2.39	4.01	4.08	2.40	3.87	4.23	2.11	0.13	0.56

the $\beta 2$ model of the Ga-rich surface [9]. The In dimers are about 10% longer and the dimer–dimer separation is about 4% larger than in case of Ga-rich surfaces. This is simply due to the covalent radius of In, which is about 14% larger than that of Ga [11]. This size difference also leads to an increase of the distance between the first two atomic layers in case of In adsorbates.

3.2. Energetics

Due to the different number of In and Ga atoms per surface unit cell the energetical comparison of the surface structural models has to take into account the In and Ga chemical potentials. Upper limits on the chemical potentials μ are set by the bulk elements [12,13]. The lower limit of μ(Ga) can be determined from

$$\mu(\mathrm{Ga}) + \mu(\mathrm{As}) = \mu(\mathrm{Ga})_{\mathrm{bulk}} + \mu(\mathrm{As})_{\mathrm{bulk}} - \Delta H_{\mathrm{f}}. \quad (1)$$

Thus, the chemical potential of the surface Ga atoms varies in the interval

$$-\Delta H_{\mathrm{f}} \le \mu(\mathrm{Ga}) - \mu(\mathrm{Ga})_{\mathrm{bulk}} =: \Delta\mu(\mathrm{Ga}) \le 0. \quad (2)$$

For the heat of formation of GaAs, ΔH_{f}, we use the experimental value of 0.74 eV [14]. We calculate a value of 0.77 eV. This gives a rough estimate for the accuracy of our calculations. The lower limit of the In chemical potential is in principle given by the extreme situation, where no indium is available in the recipient. However, the physically interesting range of μ(In) is determined by the stability of the In-covered versus the clean GaAs(001) surface.

In order to assess the energetical stability of the interface geometries we show in Fig. 2 the phase diagram of the surface in dependence on the chemical potentials of Ga and In. We find that for In- and As-rich conditions the In/GaAs(001)$\beta 2_3$ model represents the ground state of the surface. For lower values of μ(In), and depending on the value of μ(Ga), the As-rich $\beta 2(2\times 4)$, $\alpha(2\times 4)$ and Ga-rich $\beta 2(4\times 2)$ structure, respectively, represents the minimum energy configuration. As an interesting result of our total energy calculations we find that the In/GaAs(001)$\beta 2_2$ interface is unstable, independent of the Ga and In chemical potentials: The stability of the $\beta 2_2$ structure with respect to the three-In-dimer model $\beta 2_3$ is limited to In-rich and As-poor surfaces. For those conditions, however, clean Ga-rich surfaces plus additional three-dimensional In-clusters are energetically preferred. The limited stability of a two-dimensionally In-terminated GaAs surface indicated by the calculated phase diagram agrees with experimental findings by Spindt et al. [15] on the growth morphology of the In/GaAs(001) interface: From the evolution of the ultraviolet photoemission spectra with coverage they

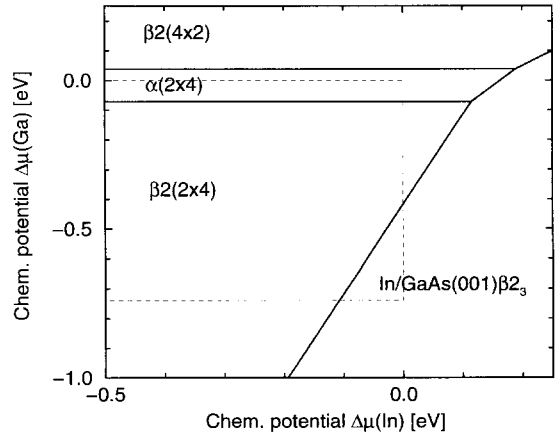

Fig. 2. Diagram of the In-induced and Ga-rich (4×2) as well as As-rich (2×4) reconstructions of the GaAs(001) surface versus the In and Ga chemical potentials. Dashed lines indicate the approximate range of thermodynamically allowed values of $\Delta\mu(i)$.

conclude on a competition between In bonding to the GaAs surface and the formation of In clusters. The surface stress induced by the relatively large In atoms is a possible explanation for the limited stability of the models investigated. We cannot, however, rule out the existence of further, different In/GaAs-interface geometries.

3.3. Electronic properties

In Fig. 3 we show the projected GaAs bulk band structure together with the bound surface states for the energetically favoured In/GaAs(001)$\beta 2_3(4 \times 2)$ interface in the energy region of the fundamental gap. The occupied surface states are below the bulk valence band maximum (VBM) as in case of the Ga-rich GaAs(001)$\beta 2(4 \times 2)$ surface [9]. The highest occupied surface state V1 (0.32 eV below the bulk VBM at K) corresponds to a bonding combination of In sp^2 hybrids between the In-dimer atoms and between the In dimers and the anions in the second atomic layer. The energetically by about 0.2 eV lower lying state V2 is mainly associated with non-bonding p orbitals localized at the three-fold coordinated second-layer As atoms and the σ bonding of the third-layer In dimer. Unoccupied surface states occur distinctly below the bulk conduction band minimum: C1 arises from a bonding combination of In p_z orbitals at the third-layer In dimer. C2 is the corresponding antibonding combination. The orbitals corresponding to the occupied and unoccupied surface bands are somewhat asymmetric with respect to the [110] direction.

Due to the structural and chemical similarity between In-induced and Ga-rich GaAs(001)(4×2) surface reconstructions we find obvious similarities also with respect to the calculated surface electronic structure (cf. Ref. [9]). This explains the RAS findings of Ref. [6], where only minor differences between the peak shapes and peak positions of the spectra measured for the clean Ga-rich and the In-terminated GaAs(001)(4×2) surfaces have been noted.

The electrostatic potential obtained during the self-consistent solution of the Kohn–Sham equations in our calculation allows to determine the energy

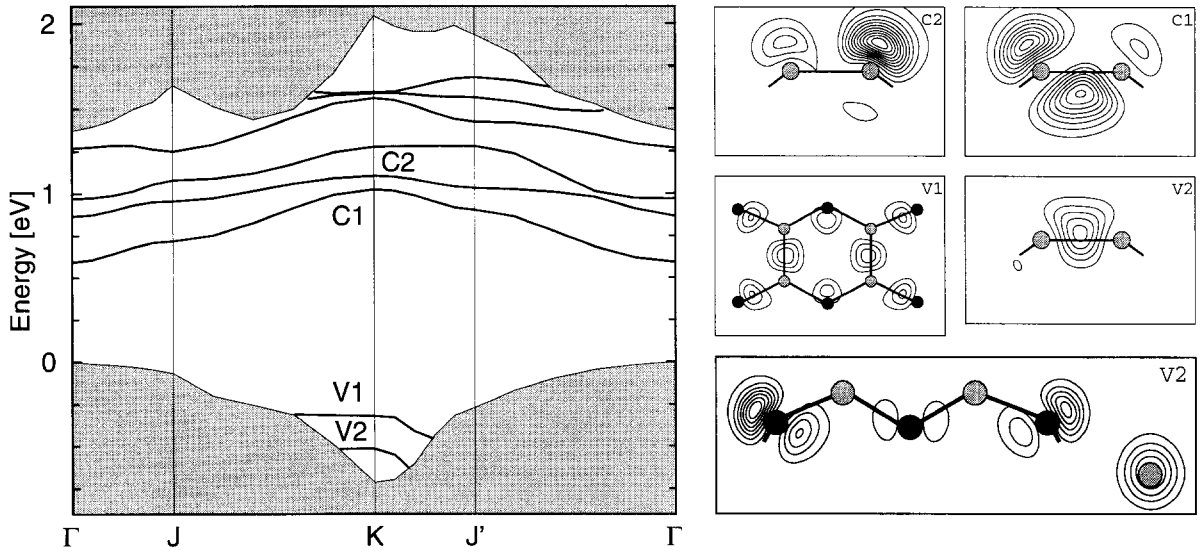

Fig. 3. Left: surface band structure (bound states) for the In/GaAs(001)$\beta 2_3(4 \times 2)$ surface. The projected GaAs bulk band structure is indicated by gray regions. Right: Contour plots of the squared wave functions at K for localized surface states. The contour spacing is 10^{-3} e/bohr^3. C2 and C1 are localized at the third-layer In-dimer. V1 is shown in a (001) plane between the first and second atomic layer. V2 is drawn along the third-layer In-dimer and in a $(\bar{1}10)$ plane cutting through the bonds between first-layer anions and second-layer anions.

barrier for an electron passing from the bulk to the vacuum region. The ionization energy I corresponds to the difference between this potential in the vacuum region and the VBM. For the Ga-rich GaAs(001)$\beta 2(2\times 4)$ surface we have calculated a value $I = 5.04$ eV [9], somewhat smaller than the measured value of 5.23 eV [16]. For the In/GaAs(001)$\beta 2_3(4\times 2)$ surface we calculate a reduction by $\Delta I = 0.38$ eV with respect to the clean Ga-rich GaAs surface. The reduction of the ionization energy can be explained by the lower electronegativity of the In adsorbate atoms compared to Ga [11].

4. Conclusions

We have performed total-energy calculations on two adsorption models for the In/GaAs(100)(4×2) interface. For As- and In-rich GaAs surfaces a interface structure with two In dimers in the top and one In dimer in the third atomic layer may explain recent experimental results. We find that the structural properties of the interface are very similar to those of the Ga-rich GaAs(4×2) reconstruction. Remaining differences are mainly due to the larger size of the overlayer cations. The analogy between Ga-rich and In-terminated surfaces holds also for the surface electronic structure. The cation-dimer bonds dominate the band structure of the In/GaAs(001)$\beta 2_3$-(4×2) surface. We observe unoccupied surface states in the upper half of the GaAs bulk band gap.

Acknowledgements

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