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(4×2) and (2×4) reconstructions of GaAs and InP(001) surfaces

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Abstract. We report results of *first-principles* total-energy calculations. The atomic and electronic structure and the formation energy of the Ga-rich GaAs(001)-β2(4 × 2) surface is compared with recent results for the As-rich GaAs(001)-(2 × 4) surface reconstructions. The relaxed β2(4 × 2) structure is characterized by an appreciable decrease of the distance between the first and second atomic layer and gives rise to unoccupied Ga-dimer-derived surface states in the upper half of the GaAs bulk band gap. Its stability is limited to extreme Ga-rich conditions. For the InP(001) surface, we investigate a series of (4 × 2) and (2 × 4) reconstructions that were suggested in order to explain recent experiments. Among these models, a structure containing three- and four-fold coordinated In atoms is energetically favourable, independent of the chemical potentials of the surface constituents.

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The (001) surfaces of III–V compound semiconductors are widely used in device applications. Molecular beam epitaxy (MBE) grown As-terminated GaAs(001)-$c(2 \times 8)/(2 \times 4)$ reconstructions have been extensively investigated (for a review see, e.g., [1]) and are fairly well understood. There is excellent agreement between recent scanning tunneling microscopy (STM) [2], X-ray diffraction [3], reflection high-energy electron diffraction (RHEED) [4], and reflectance anisotropy spectroscopy (RAS) [5] experiments with *first-principles* total-energy calculations [6–9] on the structural details of the so-called α, β, and β2 models. Also the electronic properties of the As-rich (2 × 4) reconstructions have recently been studied [10]. On the other hand, much less is known about the precise atomic and electronic structure of the Ga-rich $c(8 \times 2)/(4 \times 2)$ reconstructed GaAs(001) surface. STM [11] and low-energy electron diffraction (LEED) [12] experiments arrived at different conclusions concerning the ground state geometry of this surface. *First-principles* total-energy calculations [6, 8], however, indicate that the β2(4 × 2) structure (shown in Fig. 1) is the lowest energy configuration for the Ga-rich GaAs(001)-(4 × 2) surface. This agrees with the STM studies by Biegelsen et al. [13] and Xue and co-workers [14].

Recently much experimental work has been performed on the structural analysis of the InP(001) surfaces. By ion-sputtering and annealing, In-rich surfaces with (4 × 1) and $c(8 \times 2)/(4 \times 2)$ translational symmetry have been prepared [15–17]. Shimomura et al. [18] suggest an InP(001)-(4 × 2) structure that is based on their STM images and combines two In dimers in the third layer with an extensive In-P-intermixing in the two uppermost layers. On the other hand, Yang and Hasegawa [19] observed during the MBE a (2 × 4) reconstruction both for P- and In-rich conditions. This agrees with STM images of oxidized InP surfaces, which after heating to above 550 °C show a (2 × 4)-reconstructed surface [20]. MacPherson and co-workers [20] interprete their images in terms of a P trimer-like structure. An InP(001)-(2 × 4) reconstruction following ion bombardment and annealing has also been observed in [21]. In their time-of-flight scattering and recoiling spectrometry (TOF-SARS), Sung et al. found best agreement between experiment and simulation for a model that combines three- and four-fold coordinated In atoms in the uppermost layer with P dimers in the second atomic layer. Total-energy calculations, on the other hand, find a low-indium coverage ($\Theta = 1/4$) non-dimerized (4 × 2) surface to yield the lowest energy [22].

The aim of the present study is to contribute to a better understanding of the (4 × 2) and (2 × 4) surface reconstructions of GaAs and InP. We calculate the atomic and electronic properties of the Ga-rich GaAs(001)-β2(4 × 2) surface. The study is on the same footing as a recent investigation of the As-rich GaAs(001)-(2 × 4) reconstructions; therefore a meaningful comparison can be made. Furthermore, we compare the surface formation energies of structural models that were suggested to explain the (4 × 2) and/or (2 × 4) reconstructions of InP(001) surfaces.

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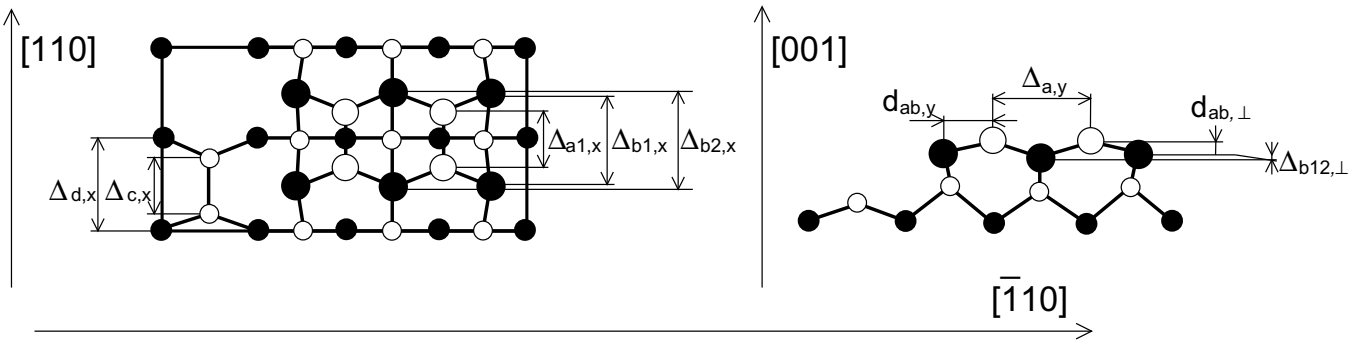

Fig. 1. Top and side view of the relaxed GaAs(100)-β2(4 × 2) surface. Large (small) empty circles indicate top (third) layer Ga atoms, whereas large (small) filled circles represent second (fourth) layer As atoms

1 Method

Our calculations are based on density-functional theory in local-density approximation (DFT-LDA). We consider an artificial periodic slab geometry along the surface normal. The unit cell includes an atomic slab with 7 atomic III–V(001)-(4 × 2) or (2 × 4) layers and a vacuum region equivalent in thickness. The cation terminated bottom layer of the slab is saturated with fractionally (Z = 1.25) charged H atoms [23]. Two layers on this side of the slab are kept frozen, whereas all other atoms are allowed to relax. 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. The electron-ion interaction is simulated by using fully separable, norm-conserving pseudopotentials [24]. For the many-body electron-electron interaction, we employ the exchange and correlation potential by Ceperley and Alder [25]. Single-particle orbitals are expanded into plane waves up to an energy cut-off of 15 Ry. ***k***-space integrations are replaced by a sum over 4 special points in the irreducible part of the surface Brillouin zone. The minimum of the total-energy functional [26] with respect to both the electronic and atomic degrees of freedom is found by means of a molecular-dynamical approach [27]. The atoms are assumed to be in their fully relaxed positions when the forces acting on the ions are smaller than 0.025 eV/Å. The calculations are performed with the theoretical equilibrium lattice constants of 5.56 Å (GaAs) and 5.67 Å (InP), which are smaller than the experimental values of 5.65 and 5.87 Å, respectively. These discrepancies between the lattice parameters obtained from DFT-LDA calculations and the measured values are typical [28] and remain, even if temperature effects are taken into account. This is mainly attributed to the missing contribution of the Ga 3*d* and In 4*d* states, which are considered as frozen-core states and therefore hidden in the pseudopotentials [29]. However, the approach and numerical parameters have proven successfully in determining the structural and dynamical properties of (110) surfaces of GaAs and InP [30].

2 Results

2.1 GaAs(001)-β2(4 × 2) *structure*

2.1.1 Atomic structure. We relaxed a series of structures with buckled and twisted dimers within the class of the β2 model in order to determine the ground-state geometry for the Ga-rich GaAs(001)-(4 × 2) surface. The optimized geometry is shown in Fig. 1. Table 1 contains the corresponding structural parameters (geometry parameters given in this work refer to the calculated equilibrium lattice constants).

The minimum-energy configuration has nearly symmetric Ga dimers. The largest dimer buckling of about 0.02 Å occurs in the third atomic layer. The Ga-dimer lengths $\Delta_{a1,x}$, $\Delta_{c,x}$ are about 2.4 Å and are therefore somewhat smaller than the sum of the Ga covalent radii (2.52 Å [31]). The cation dimers are also shorter than the anion dimers on As-rich surfaces (cf. Table 1). This already indicates different bonding mechanisms for anion and cation dimers as will be explained below. Our calculated Ga-dimer length deviates significantly from the LEED results in [12] with reports of 2.13 and 3.45 Å; it agrees, however, with previous *first-principles* calculations [6, 8].

The three-fold coordinated Ga-dimer atoms prefer a nearly planar, sp^2-like bonding situation. The three-fold coordinated As-atoms in the second atomic layer, on the other hand, move into a pyramidal configuration with their three cation neighbours. This relaxation of surface Ga and As atoms is analogous to the buckling of the GaAs(110) surface and has also been observed for the As-rich GaAs(001) surfaces [9]. As a result we find the minimum interplanar distance $d_{ab,\perp}$ between first and second layer to be reduced to 0.46 Å. This is in sharp contrast to the dimer steepening of the As-terminated GaAs(001) surfaces. Also the displacements of the second-layer anions can be explained by the tendency of the Ga-dimer atoms towards a planar bonding. As a result of the cation-dimer formation the three-fold coordinated anions are pushed away laterally by about 0.3 Å.

Table 1. Geometrical parameters in Å of the relaxed GaAs(001)-β2(4 × 2) surface (cf.Fig. 1)[a]

	$\Delta_{a1,x}$	$\Delta_{b1,x}$	$\Delta_{b2,x}$	$\Delta_{c,x}$	$\Delta_{d,x}$	$\Delta_{a,y}$	$d_{ab,y}$	$\Delta_{b12,\perp}$	$d_{ab,\perp}$
GaAs(001)-β2(4 × 2)	2.39	4.01	4.08	2.40	3.87	4.23	2.11	0.13	0.56
GaAs(001)-β2(2 × 4)	2.50	3.65	3.52	2.52	3.70	3.82	1.42	−0.28	1.49

[a] For comparison the corresponding values for the GaAs(001)-β2(2 × 4) surface from [9] are given

2.1.2 Formation energy. In order to compare energetically the GaAs(001)-β2(4 × 2) surface with other GaAs(001) surfaces, one has to take into account the chemical potentials $\mu(A_i)$ of the surface constituents Ga and As. The ground state of the surface is determined by the minimum of the thermodynamic potential

$$\Omega = U - TS - \sum_i \mu(A_i) n_{A_i} . \quad (1)$$

U is the total energy of the system. The entropy term, TS, contributes very little to the difference in Ω for various structures under usual experimental conditions and is neglected (for a more detailed discussion see, e.g., [32]). The chemical potentials $\mu(A_i)$ are restricted by

$$\mu(A_i) \leq \mu(A_i)_{\text{bulk}} . \quad (2)$$

Furthermore, they are related to each other by

$$\begin{aligned} \mu(\text{Ga}) + \mu(\text{As}) &= \mu(\text{GaAs})_{\text{bulk}} \\ &= \mu(\text{Ga})_{\text{bulk}} + \mu(\text{As})_{\text{bulk}} - \Delta H_f(\text{GaAs}) , \end{aligned} \quad (3)$$

with ΔH_f(GaAs) being the heat of formation of GaAs. Consequently, the formation energy may be written as a function of a single variable, which we will take to be $\Delta\mu$(As):

$$-\Delta H_f(\text{GaAs}) \leq \Delta\mu(\text{As}) := \mu(\text{As}) - \mu(\text{As})_{\text{bulk}} \leq 0 . \quad (4)$$

For the heat of formation, ΔH_f(GaAs), we calculate a value of 0.77 eV. Experimental values amount to 0.74 [33], 0.84, and 0.94 eV [34]. This gives a rough estimate for the accuracy of the calculations. In Fig. 2, we compare the calculated formation energy of the Ga-rich GaAs(001)-β2(4 × 2) structure vs. the As chemical potential with As-rich GaAs(001)-(2 × 4) structures calculated earlier [10]. Obviously the GaAs(001)-β2(4 × 2) structure may be stable only in a very small range of the surface chemical potentials for extreme Ga-rich preparation conditions. This agrees with the phase diagram measured by Däweritz and Hey [35]. It may also explain the finding that during cooling of GaAs(001) samples, the As-stabilized surface structure is reestablished from a Ga-stabilized one by surface segregation of excess arsenic from the bulk [1].

2.1.3 Electronic properties. In Fig. 3, we show the projected GaAs bulk band structure together with the bound surface states for GaAs(001)-β2(4 × 2) 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 As-rich GaAs(001)-β2(2 × 4) surface [10]. The highest occupied surface state $V1$ (0.18 eV below the bulk VBM at K) corresponds to a bonding combination of Ga sp^2 hybrids between the Ga-dimer atoms and between the Ga dimers and the anions in the second atomic layer. The energetically lower lying states $V2$ and $V3$ are associated with non-bonding p orbitals localized at the three-fold coordinated second-layer As atoms. Unoccupied surface states occur distinctly below the bulk conduction band minimum (CBM), in contrast to the As-rich (2 × 4) surfaces. $C1$ arises from a bonding combination of Ga p_z orbitals at the third-layer Ga dimer. $C3$ is the corresponding antibonding combination. $C2$ and $C4$ correspond

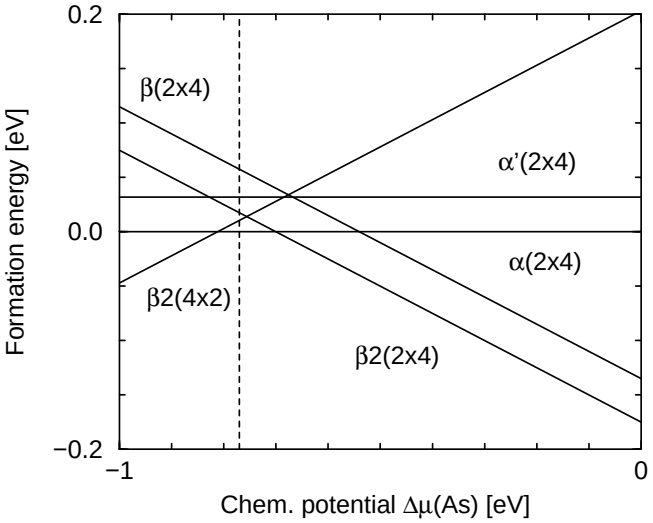

Fig. 2. Formation energy per (1 × 1) unit cell for GaAs(001)(4 × 2) and (2 × 4) reconstructed surfaces relative to the α(2 × 4) phase (cf. [10]) as a function of $\Delta\mu$(As) over the thermodynamically allowed range $-\Delta H_f \leq \Delta\mu(\text{As}) \leq 0$. The dashed line indicates the calculated position of $-\Delta H_f$

to bonding and antibonding combinations of Ga p_z orbitals at the uppermost Ga atoms. The orbitals corresponding to the occupied and unoccupied surface bands are slightly asymmetric with respect to the [110] direction. This agrees with the findings of Ohno [36].

The band structure presented here suffers from the well-known DFT-LDA gap problem, i.e., underestimated excitation energies. The inclusion of many-body effects leads to a considerable improvement. In particular, empty surface states are shifted more than empty bulk states towards higher energies [37, 38]. On the other hand, the underestimation of the equilibrium lattice constant and the neglect of the relaxation of the Ga 3d electrons [39] in our calculation lead to a widening of the fundamental gap that roughly compensates for the underestimation of the excitation energies within DFT-LDA. Nevertheless, we expect the unoccupied surface states to change somewhat their position with respect to the projected bulk band structure.

The formation of the Ga-dimer bond is schematically explained in Fig. 4. Slightly below the bulk VBM, we observe occupied σ bonds, formed by Ga sp^2 hybrids. π bonding combinations of Ga p_z orbitals lie energetically in the upper half of the GaAs band gap. These π bonds form the lowest unoccupied surface state. π* antibonding combinations of Ga p_z orbitals and σ* antibonding combinations of Ga sp^2 hybrids lie above the bulk CBM. It is interesting to note that the bonding of the cation dimers on GaAs(001) surfaces is quite similar to the formation of symmetric Carbon dimers on the diamond (001) surface [38]. On the diamond surface, however, both σ and π bonds are occupied due to the higher valence of the C atoms. The mechanism of the Ga dimerization is somewhat different from that observed for As dimers at As-rich GaAs(001) surfaces [10]: In the latter case the highest occupied surface state close to the bulk VBM is associated with a π* antibonding combination of As p_z orbitals. In the case of As dimers, a nearly complete dehybridization occurs and the σ and σ* combinations are formed by As p orbitals polarized along the dimer direction. The $pp\sigma^*$ As-

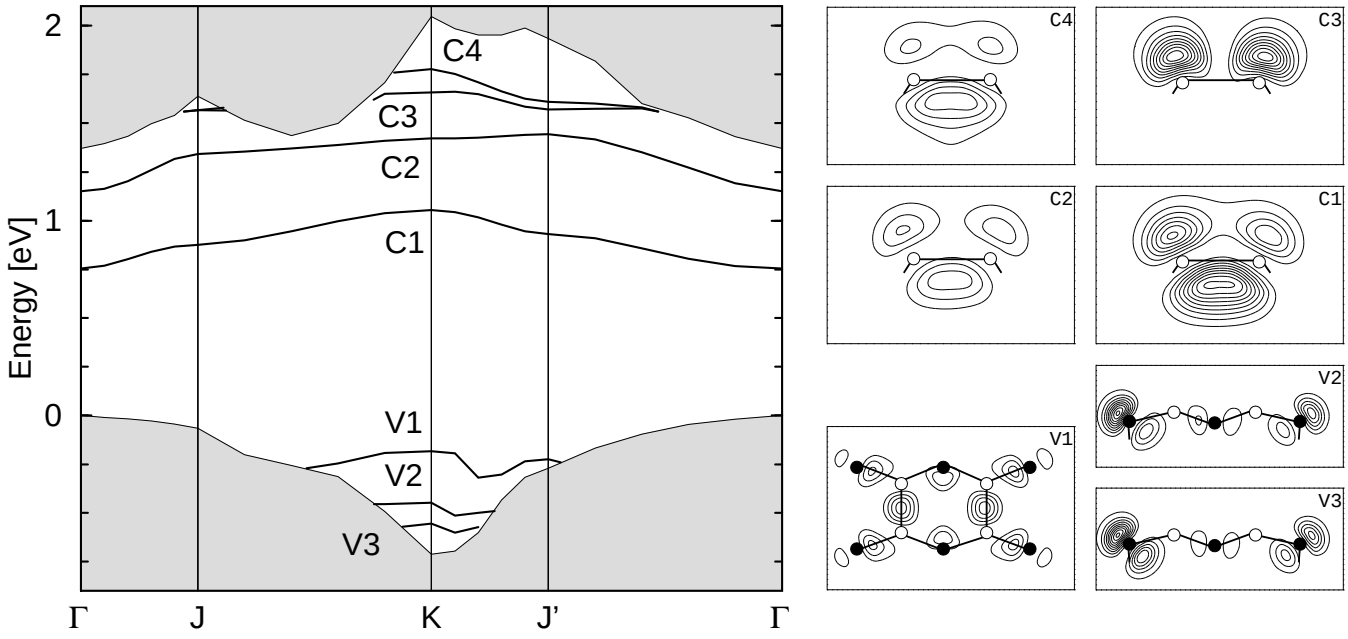

Fig. 3. *Left:* surface band structure (bound states) for the GaAs(001)-β2(4 × 2) surface. The projected GaAs bulk band structure is indicated by gray regions. *Right:* Contour plots of the squared wave functions at K for localized surface states. The contour spacing is $10^{-3}\ e/\mathrm{bohr}^3$. $C4$ and $C2$ ($C3$ and $C1$) are localized at the uppermost (third-layer) Ga-dimers. $V1$ is shown in a (001) plane between the first and second atomic layer. $V2$ ($V3$) is drawn in a $(\bar{1}10)$ plane cutting through the bonds between first-layer anions and second-layer anions which cuts (does not cut) the third-layer Ga dimer

dimer bond lies energetically slightly above the bulk CBM. The different bonding mechanisms for Ga and As dimers are responsible for the structural differences between Ga- and As-rich GaAs(001) surfaces discussed above.

The electrostatic potential obtained during the self-consistent solution of the Kohn–Sham equations in our calculation allows to determine the energy 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 As-rich GaAs(001)-β2(2 × 4) surface, we have calculated a value $I = 5.43$ eV [10] close to the measured values for the ionization energy of 5.5 [40] or 5.62 eV [41]. The good agreement between calculated and measured ionization energies maybe somewhat fortuitous. However, differences between ionization energies of different surface structures can be calculated with high accuracy within DFT-LDA [42, 43]. For the Ga-rich GaAs(001)-β2(4 × 2) surface, we calculate a reduction $\Delta I = 0.39$ eV with respect to the value for the As-rich β2(2 × 4) surface. This value is in perfect agreement with the measured reduction of the ionization energy of 0.39 eV [41]. The reduction of the ionization energy can be explained by the formation of a surface dipole between surface anions and cations.

2.2 InP(001) *surface*

2.2.1 Formation energy. We investigated a series of InP(001)-(4 × 2) and (2 × 4) reconstructions, which were suggested in order to explain the surface structure. In particular we relaxed six structural models: These are (i) the β2(4 × 2) structure analogous to the model for the Ga-rich GaAs(001)-(4 × 2) surface, (ii) the (4 × 2) surface structure suggested by Shimomura and co-workers [18], (iii) the (4 × 2) model favoured in the total-energy calculations by Jin et al. [22], (iv) the (2 × 4) P-trimer structure suggested by MacPherson [20], (v) the (2 × 4) combination of P dimers with three- and four-fold coordinated In atoms suggested by Sung and co-workers [21], and (vi) a model proposed by Esser et al. [44], which arranges one first-layer and two third-layer In dimers in a (2 × 4) surface unit cell. These structures realize different In coverages of $\Theta = 1/4$ (Jin-Model), $\Theta = 1/2$ (MacPherson-Model), $\Theta = 3/4$ (β2 structure, Sung-Model, Esser-Model), and $\Theta = 1$ (Shimomura-Model) and can therefore only by compared by taking into account the chemical potentials of the surface constituents. Nevertheless, both for In-rich as well as for P-rich conditions, we find the (2 × 4) structure suggested by Sung et al. on grounds of their TOF-SARS study [21] to describe the surface ground state (Fig. 5). The (2 × 4) dimer reconstruction model by Esser and co-workers [44] is about 0.04 eV higher in energy. This energy separation is comparable to that calculated for the β and β2 phases of the

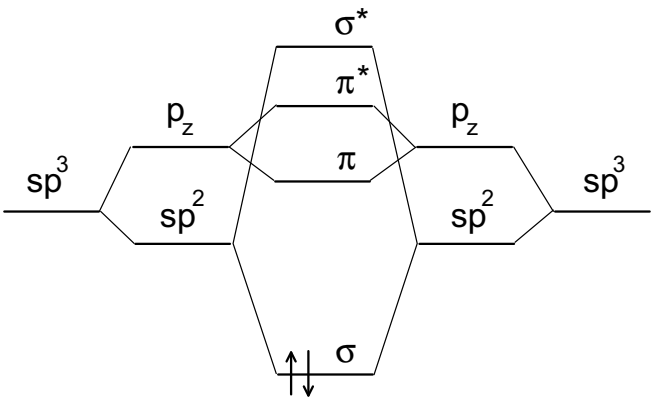

Fig. 4. Schematic energy diagram of Ga dimers on GaAs(001) surfaces

GaAs(001)-(2×4) surface [6, 8, 9]. The InP(001)-$\beta2(4\times2)$ structure is the most favourable (4×2) surface reconstruction among the models investigated. Its energy is about 0.09 eV higher than that of the Sung-Model. Therefore it can safely be excluded to be an equilibrium structure. It is interesting to note that the only model investigated that does not satisfy electron counting heuristics [45], namely, the structure proposed by Jin and Lewis [22], is energetically the most unfavourable structure. This indicates the validity of the electron counting rule for InP(001) surfaces.

2.2.2 Atomic structure. The relaxed geometry of the minimum energy structure within the range of the investigated models for the InP(001) surface is shown in Fig. 5. The Sung-Model is characterized by a dimerization of the exposed second-layer P atoms. The calculated P-dimer length amounts to 2.23 Å. This is only slightly larger than the sum of the P covalent radii of 2.12 Å [31], but much smaller than the measured value of 2.95 ± 0.20 Å [21]. For the In-In bond length in the uppermost layer, we determine a value of 2.80 Å, which again is close to sum of the corresponding covalent radii (2.88 Å [31]), but much smaller than the interatomic distance of 3.65 ± 0.20 Å found experimentally [21]. The conservation of nearly ideal bond lengths for the relaxed Sung-Model may explain the energetical stability of the structure. On the other hand, the bond angle between the uppermost In atom and its cation neighbours deviates appreciably from the ideal tetrahedral angle. Obviously the conservation of bond angles is less important in the energy balance of the InP surface. A partially metallic bond character as observed for monolayer Al adsorption on GaAs(110) [46] could be a possible explanation. In order to fully explain the stability of the Sung-Model investigations of the surface electronic structure are needed and presently underway. However, already at this stage we can speculate that the large size difference between cation and anion in InP is the reason for the In-dimer reconstructions to be energetically unfavourable. The In dimers on InP surfaces cause probably too much stress in the second atomic layer in contrast to GaAs, where Ga dimers can still be accomodated on the surface.

3 Summary

We performed *first-principles* total-energy calculations of (4×2) and (2×4) reconstructions for GaAs and InP(001) surfaces. We find appreciable differences between the geometries of the Ga-rich GaAs(001)-$\beta2(4\times2)$ surface and the corresponding As-rich GaAs(001)-$\beta2(2\times4)$ structure. These differences can be traced back to different mechanisms for cation- and anion-dimer formation. The cation-dimer bonds dominate the band structure of the GaAs(001)-$\beta2(4\times2)$ surface. We observe unoccupied surface states in the upper half of the GaAs bulk band gap. A completely different reconstruction mechanism seems to be responsible for the formation of the InP(001)-(2×4) surface. This is probably related to the larger geometric inequivalence of the substrate constituents in case of InP. Both for In- and P-rich conditions, we find a structure with three- and four-fold coordinated In atoms in the first and P dimers in the second atomic layer to be stable.

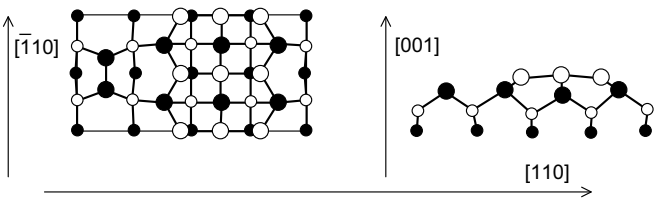

Fig. 5. Top and side view of the relaxed InP(100)-(2×4) surface (Sung-Model [21]). Large (small) empty circles represent first (third) layer In atoms, whereas large (small) filled circles indicate second (fourth) layer P atoms

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