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Geometry and electronic structure of GaAs(001)(2×4) reconstructions

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Structural and electronic properties of the As-rich GaAs(001)(2×4) reconstructions are investigated by means of converged *first-principles* total-energy calculations. For an As coverage of $\Theta=3/4$, we find the two-dimer $\beta 2$ phase to be energetically preferred over the three-dimer β phase. As the As chemical potential decreases, the α phase of GaAs(001) represents the ground state of the surface. All geometries are characterized by similar structural elements as As dimers with a length of about 2.5 Å, dimer vacancies, and a nearly planar configuration of the threefold-coordinated second-layer Ga atoms leading to a steepening of the dimer block. Consequently, the resulting electronic properties also have similar features. The surface band structures are dominated by filled As-dimer states and empty Ga dangling bonds close to the bulk valence- and conduction-band edge, respectively. The measured Fermi-level pinning cannot be related to intrinsic surface states. The calculated surface states and ionization energies support the $\beta 2$ structure as the surface geometry for an As coverage of $\Theta=3/4$. [S0163-1829(96)04248-8]

I. INTRODUCTION

The GaAs(001) surface is one of the most studied polar semiconductor surfaces and has attracted much interest of both experimentalists and theoreticians because of its importance for the growth of multilayer device structures. As-rich $(2\times4)/c(2\times8)$ reconstructions, in which the surface is mainly terminated by various arrangements of As dimers are most important in molecular-beam epitaxy (MBE) of GaAs-based layered structures.

Three different phases of the 2×4 surface have been identified by reflection high-energy electron-diffraction experiments.[1–3] The α, β, and γ phases correspond to a characteristic ratio of fractional order intensities. On grounds of a comparison with scanning tunneling microscopy (STM) images, Hashizume *et al.*[2,3] concluded that all three phases have the same outermost surface layer of the unit cell, which consists of two As dimers and two dimer vacancies. The α phase is described by the two-dimer model of Farrel and Palmstrøm[1] with a significant relaxation of the second-layer Ga atoms (cf. Fig. 1). The β phase corresponds to the two-dimer model originally introduced by Chadi,[4] which is characterized by an additional As dimer in the third layer. According to the notation of Northrup and Froyen,[5] this structure will be called $\beta 2$ in the following (cf. Fig. 1). The γ phase was found to be a mixture of the β phase and the $c(4\times4)$ phase with the surface As coverage varying depending on the actual growth conditions. On the other hand, three and two As dimers in the outermost surface layer in 2×4 unit cells are seemingly observed by STM (Refs. 6–8) and explained by the β and α structures shown in Fig. 1. Both the three-dimer β structure and the two-dimer $\beta 2$ structure correspond to the same As coverage of $\Theta=3/4$. *Ab initio* calculations by Ohno[9] and Northrup and Froyen[5] came to opposite conclusions concerning their energetical stability. Also the atomic structure of the α phase is not clear. Northrup and Froyen[5] observed a dimerization of the second-layer Ga atoms in agreement with the early prediction by Chadi,[4] but in contrast to Ohno,[9] who ruled out a Ga-Ga bonding for the α phase. There is also a lack of consensus on other structural details. Recent STM studies[8] indicated an apparent twisting of the As dimers in the α structure. However, symmetric dimers are found to be in best agreement with x-ray photoelectron diffraction (XPD) data.[10] A rather wide range of As-As dimer bond lengths is reported. XPD studies[10] indicate a dimer length of 2.2 Å, energy-dependent photoelectron diffraction experiments[11] determined a value of 2.4 Å, and secondary-ion mass spectrometry investigations[12] found the As dimer atoms to be 2.73 Å apart. An early theoretical study[13] considering As-As dimers in 2×1 surface unit cells predicts a dimer length of 2.52 Å. Recent *ab initio* calculations[14,15] state values of 2.39 and 2.60 Å, respectively. Other structural parameters as interplanar distances and relaxations in deeper layers are even less well known than the precise dimer length and symmetry.

Relatively little is known about the electronic structure of the GaAs(001) surface. The 2×4 reconstruction models considered in this work satisfy the electron counting rule, i.e., the dangling bonds are filled on surface anions and are empty at surface cations.[16] The surface band structure should be semiconducting rather than metallic since there exists no partly occupied surface state. However, work function measurements[17] on p- and n-type samples indicate a Fermi-level pinning. Irrespective of the type of reconstruction the Fermi level lies about 0.5 ± 0.1 eV above the valence-band maximum (VBM).[18] Defects, in particular kinks, were made responsible for the band bending.[19] In contrast to the constant Fermi-level position for the different phases, a small dependence of the ionization energy on the reconstruction model was observed.[20] It assumes its maximum for the β phase of the GaAs(001)(2×4) reconstructions. The occupied surface bands of the (2×4) reconstruction have been mapped by angle-resolved photoemission spectroscopy (ARPES).[21,22] Larsen *et al.* found weakly dispersive states with sp_z character in the energy range 0.5–1.6 eV below the VBM and a nearly dispersionless state near -3 eV. By applying the scattering theoretical method based on an empirical tight-binding (TB) scheme, these features were attributed to asymmetric

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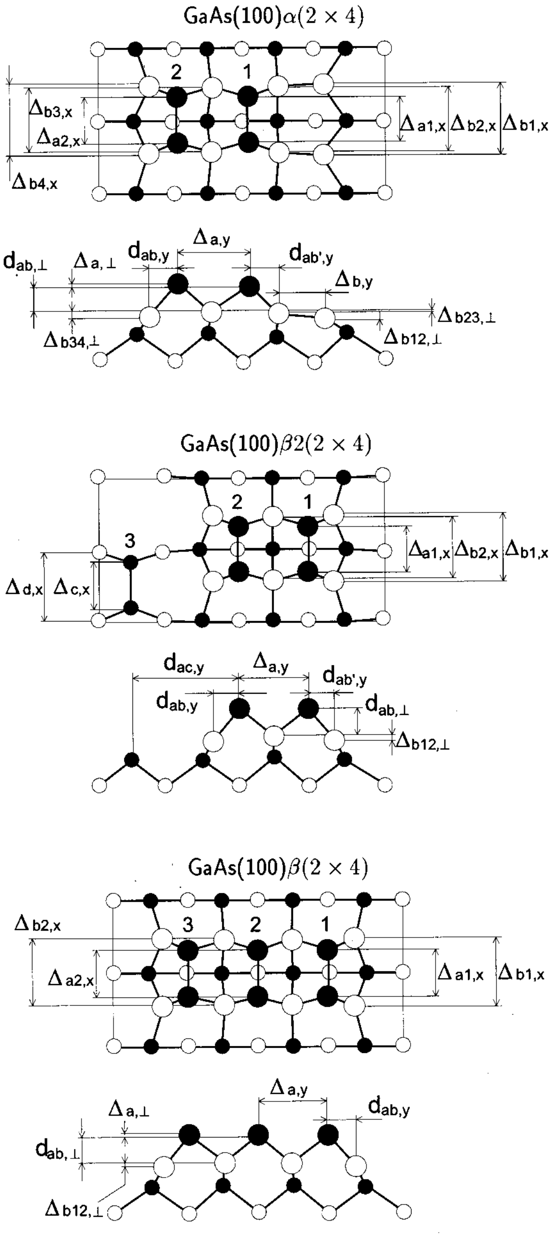

FIG. 1. Top and side views of the relaxed GaAs(001)(2×4) α, β2, and β phases. Large (small) filled circles indicate top- (third-) layer As atoms, whereas large (small) empty circles represent second- (fourth-) layer Ga atoms.

As-As dimers.[22] However, in this study as well as in several later pseudopotential[23] and TB calculations[24] the 2×4 surface reconstruction is simulated by using smaller periodicities. A more recent, parameter-free TB calculation for the GaAs(001)β(2×4) structure predicts a Fermi-level pinning between peaks associated with the lone pairs of the central As dimer of the surface and the Ga dangling bonds, respectively.[25] In order to open a semiconductorlike energy gap Rincón and co-workers[25] propose to replace an As atom of the central dimer by a Ga atom. Such a mixed composition of the uppermost surface layer has already been suggested by Falta *et al.*[26] in order to explain their ion-scattering experiments.

In this work we present results of converged *first-principles* calculations of the atomic structures and energetical ordering of the α, β, and β2 phases of GaAs(001)(2×4). Comprehensive sets of geometrical data are given for structures widely used to explain the As-rich (2×4)/*c*(2×8) reconstructions. Based on the relaxed geometries, we analyze the bound surface states and determine the ionization energies for these structures.

II. METHOD

Our calculations are based on the density-functional theory (DFT) in the local-density approximation (LDA). We consider an artificial periodic slab geometry along the surface normal. The unit cell includes an atomic slab with eight atomic GaAs(001)(2×4) layers and a vacuum region equivalent in thickness. The Ga-terminated surface of the slab is saturated with fractionally ($Z=1.25$) charged H atoms.[27] The two bottom layers on this side of the slab are kept frozen, whereas all other atoms are allowed to relax. We account for the electric field caused by the two inequivalent surfaces of the slab by applying a dipole correction[28] to the self-consistently calculated electrostatic potential. The electron-ion interaction is simulated by using fully separable, norm-conserving pseudopotentials.[29] For the many-particle electron-electron interaction we employ the exchange and correlation potential by Ceperley and Alder.[30] Single-particle orbitals are expanded into plane waves up to an energy cutoff of 15 Ry. **k**-space integrations are replaced by a sum over a set of special points,[31] corresponding to eight points in the full two-dimensional surface Brillouin zone. The minimum of the total-energy functional[32] with respect to both the electronic and atomic degrees of freedom is found by means of a molecular-dynamical approach.[28] 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. We perform the calculations with the theoretical equilibrium lattice constant of 5.56 Å, which is 1.7% smaller than the experimental value. This approach and numerical parameters have proven successful in determining precisely the structural and dynamical properties of GaAs(110) surfaces.[33]

III. RESULTS

A. Atomic structures

In order to determine the ground-state geometries for the different phases of GaAs(001) considered we relaxed a series of structures with buckled and twisted dimers. The minimum-energy configuration corresponds to symmetric As dimers in the case of α and β structures. For the β2 phase we observe a slight dimer buckling of 0.02 Å. The optimized structures for the α, β2, and β phases of GaAs(001)(2×4) are shown in Fig. 1. Their key structural data are compiled in Table I. The structures have a number of features in common. The dimer length for the topmost As dimers amounts to 2.50 Å for all three reconstruction models. The third-layer As dimer occurring for β2 has a length of 2.52 A. The dimer lengths are very close to the bond distance of 2.51 Å found for bulk As where there is threefold coordination.[34]

The threefold-coordinated second-layer Ga atoms bonded to As dimer atoms prefer a nearly planar, sp^2-like bonding

TABLE I. Geometrical parameters (in angstroms) of the relaxed GaAs(001)(2×4) α, $\beta2$, and β structures according to Fig. 1.

GaAs(001)(2×4)	α	$\beta2$	β
$\Delta_{a1,x}$	2.50	2.50	2.50
$\Delta_{a2,x}$	2.50		2.50
$\Delta_{b1,x}$	3.85	3.65	3.65
$\Delta_{b2,x}$	3.64	3.52	3.49
$\Delta_{b3,x}$	3.50		
$\Delta_{b4,x}$	3.66		
$\Delta_{c,x}$		2.52	
$\Delta_{d,x}$		3.70	
$\Delta_{a,y}$	3.92	3.82	3.80
$\Delta_{b,y}$	2.50		
$d_{ab,y}$	1.50	1.41	1.42
$d_{ab',y}$	1.73	1.44	
$d_{ac,y}$		5.92	
$\Delta_{a,\perp}$	0.06		0.02
$\Delta_{b12,\perp}$	0.20	0.28	0.24
$\Delta_{b23,\perp}$	0.19		
$\Delta_{b34,\perp}$	0.22		
$d_{ab,\perp}$	1.42	1.49	1.47

situation. On average they are displaced from their ideal lateral position by about 0.65 Å towards the As dimers. This leads to an upward movement of the As dimers, causing the dimer block to steepen. This relaxation of surface Ga and As atoms is analogous to the buckling of the GaAs(110) surface. As a result of the dimer steepening we find the minimum interplanar distance $d_{ab,\perp}$ between first and second layer to be 1.42–1.49 Å (cf. Table I), which is slightly larger than the ideal bulk spacing of 1.39 Å. The bond length between the threefold-coordinated second-layer Ga atoms and the As dimer atoms is 2.32–2.34 Å, somewhat shorter than the ideal bulk bond length of 2.41 Å. The latter value, however, essentially is preserved in the bonds between the As dimer atoms and the fourfold-coordinated cations below. Such a bimodal Ga-As bond length distribution between the top and second layers has also been found in a recent study by Srivastava and Jenkins.[14] However, there are a number of quantitative differences between this study and the present work. They may be due to a relatively small basis set and the four-layer slab used in Ref. 14. We observe an appreciable buckling of up to 0.44 Å even in the fourth layer, indicating the need for a larger slab.

The dimer-dimer distance along the ×4 periodicity amounts to 3.8–3.9 Å and is thus slightly smaller than the according value at the ideal bulk truncated surface. The further separation of the dimers in the two-dimer α structure compared to the three-dimer block (cf. Table I) is in agreement with recent STM results.[8] Controversy exists in the theoretical predictions concerning the second-layer atomic structure of the α phase as discussed in the Introduction. Our results support the occurrence of a distinct Ga-Ga bond in the second layer with a bond length of 2.51 Å, close to sum of the Ga covalent radii (2.52 Å after Ref. 35). Such a bonding of the originally twofold-coordinated second-layer cations is consistent with electron counting heuristics.[16] It allows the acceptorlike states to be completely filled and the donorlike states to be empty.

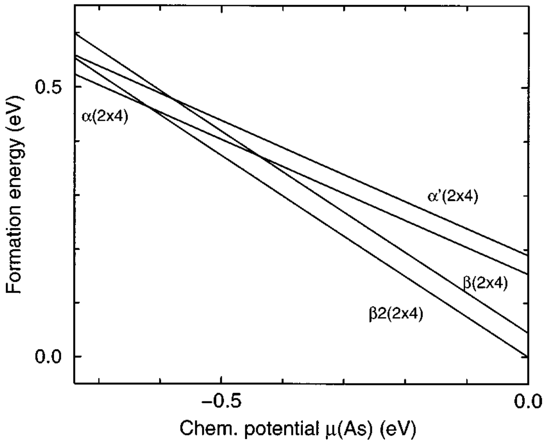

FIG. 2. Formation energy per (1×1) unit cell for GaAs(001)(2×4) reconstructed surfaces as a function of μ(As) over the thermodynamically allowed range $-\Delta H_f \leq \mu(\mathrm{As}) - \mu(\mathrm{As})_{\mathrm{bulk}} \leq 0$, where $H_f = 0.74$ eV (Ref. 36) is the heat of formation of GaAs.

B. Formation energy

Previous theoretical works[5,9] differ in their conclusions concerning the energy ordering of the GaAs(001)(2×4) reconstructions. These reconstructions have different stoichiometries. The ground state of the surface, i.e., the structure that minimizes the surface energy, therefore depends on the deposition conditions during growth or surface preparation. The stability of a certain structure may be determined from the free energy and the chemical potentials $\mu(i)$ of the surface constituents Ga and As. If the surface is in equilibrium with the bulk, pairs of Ga and As atoms can be exchanged with the bulk, for which the energy is the total bulk energy per pair. This requires that the sum of μ(As) and μ(Ga) equals this bulk quantity. Consequently, the formation energy may be written as a function of a single variable, which we will take to be μ(As). The maximum value for μ(As) corresponds to the As chemical potential of the bulk elemental phase. The lower limit is given by the As bulk chemical potential reduced by the heat of formation ΔH_f of GaAs (for a more detailed discussion see, e.g., Ref. 13). Thus the As chemical potential is restricted to a certain range

$$-\Delta H_f \leq \mu(\mathrm{As}) - \mu(\mathrm{As})_{\mathrm{bulk}} \leq 0. \qquad (1)$$

Our results for the formation energies of the different models versus the allowed range of μ(As) are shown in Fig. 2. They confirm the findings by Northrup and Froyen.[5] The α structure is stable in a limited range of the As chemical potential. Under As-rich conditions, i.e., for higher values of the As chemical potential, the α structure becomes unstable with respect to the $\beta2$ structure. We evaluate the β(2×4) structure to be 0.045 eV per 1×1 unit cell higher in energy than the $\beta2$ model. We mention that a slight asymmetry of the $\beta2$(2×4) model is energetically more favorable than a complete mirror symmetry perpendicular to the dimer direction. A small shift of the two-dimer block with respect to the third-layer dimer of about 0.07 Å accompanied by slight asymmetries in the layers below lowers the energy considerably by 0.095 eV. This value equals roughly the energy difference between the findings of Refs. 9 and 5 and may perhaps provide an explanation for their contradicting outcome. The energetical preference of the two-dimer $\beta2$ structure over the three-dimer β structure seems to contradict STM findings[6–8] with reports of two- and three-dimer structures. A high-energy barrier for the transformation of a β into a $\beta2$ structure and the kinetics of the preparation process could be possible explanations for the coexistence of both structures. Very recently it has been shown that defects may also stabilize a certain structure at the GaAs(001) surface.[37]

The higher Madelung energy of the β structure makes this geometry less stable than the $\beta2$ structure as shown in Ref. 5. The energy difference is due to the existence of a relatively large negatively charged subunit (the three-dimer block) in the 2×4 cell of the β structure. The surface charge is more homogeneously distributed in case of the $\beta2$ structure. Another possibility for a more favorable charge arrangement is the partial replacement of As by Ga atoms in the outermost layer. Such a mixed composition is not only plausible from energetical considerations, but also is reported to have been observed in ion scattering experiments.[26] The electron counting rule does not distinguish between structures in which a threefold-coordinated As atom (with a doubly occupied dangling bond) is replaced by a Ga atom (with an empty dangling bond but two valence electrons less). We perform calculations for a modified $\beta(2\times4)$ structure, where the As-As dimer in the middle of the dimer block has been replaced by an As-Ga pair. This model has been proposed in Ref. 25. The arsenic coverage of such a structure is $\Theta=1/2$ as in the case of the $\alpha(2\times4)$ model. We call this structure α'. The energy for the relaxed α' model is 0.035 eV per 1×1 surface unit cell higher than for the α structure. The energy difference is comparable to the one found between the β and $\beta2$ structures. It allows one to exclude such a mixing (at least the particular geometry studied here) from the range of possible equilibrium structures. However, since the energy difference is not large, such structures may be observed during the MBE growth with varying surface concentrations of As and Ga. Structural data for the relaxed α' model can be found in Ref. 38.

C. Electronic properties

In Fig. 3 we show the projected GaAs bulk band structure together with the bound surface states for GaAs(001)$\alpha(2\times4)$ in the energy region of the fundamental gap. The gap is essentially free of surface induced states. Slightly above the bulk VBM (0.16 eV at K) we find the highest occupied state $V1$. This only weakly dispersive feature corresponds to an antibonding π^* combination of the p_z orbitals localized at the As dimer 1 (cf. Fig. 4, the notation of the dimers is according to Fig. 1). The corresponding bonding π combination at dimer 1 gives rise to $V2$ and is about 0.3 eV lower in energy. $V3$ is related to an antibonding π^* combination of p_z orbitals at dimer 2. $V4$ and $V5$ are nearly degenerate and lie about 0.6 eV below the VBM. These very flat states arise from σ-type As-Ga bonds between the third and fourth ($V4$) and beween the first and second ($V5$) atomic layers, respectively (cf. Fig. 4). The lowest unoccupied states $C1$ and $C2$ are related to empty Ga dangling bonds located at threefold-coordinated second-layer Ga atoms. They are slightly below and above the conduction-band minimum (CBM).

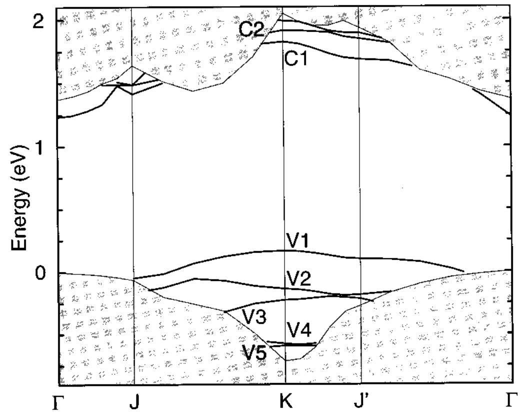

FIG. 3. Surface band structure (bound states) for GaAs(001)$\alpha(2\times4)$ plotted over the projected bulk band structure (gray regions).

In case of the GaAs(001)$\beta2(2\times4)$ structure all occupied surface bands are below the VBM (cf. Fig. 5). The two highest occupied states $V1$ and $V2$ lie 0.26 and 0.35 eV below VBM at K, respectively. They correspond to antibonding π^* combinations of p_z orbitals located at the third-layer ($V1$) and top-layer ($V2$) As dimers as shown in Fig. 6. The π bonding of the third-layer and top-layer As dimers give rise to $V3$ and $V4$, respectively. In contrast to the α structure discussed above, we find that the states localized at the top-layer dimers show nearly identical charge distribution at dimers 1 and 2 (cf. the notation of the dimers in Fig. 1). The small symmetry break in $\times4$ direction observed for the

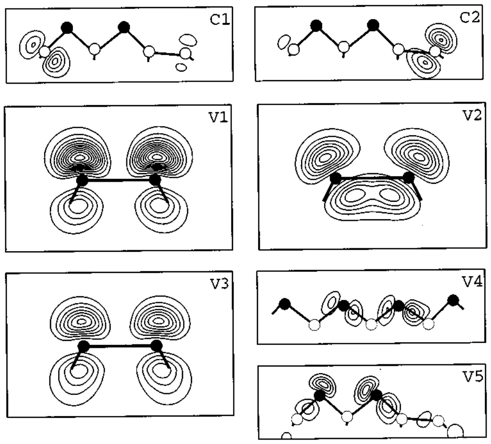

FIG. 4. Contour plots of the squared wave functions at K for surface localized states of the GaAs(001)$\alpha(2\times4)$ surface. The contour spacing is $10^{-3}e$ bohr^{-3}. All plots are drawn parallel to the surface normal. $C1$, $C2$, and $V5$ are plotted along a plane parallel to the $\times4$ direction cutting through the bonds between first-layer anions and second-layer cations. $V1$ and $V2$ ($V3$) are localized at dimer 1 (2) (cf. Fig. 1). $V4$ is the charge density along the bonds between third-layer As and fourth-layer Ga underneath the surface dimers.

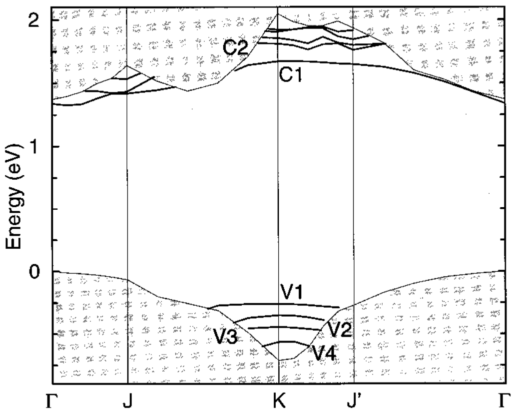

FIG. 5. Surface band structure (bound states) for GaAs(001)$\beta2(2\times4)$ plotted over the projected bulk band structure (gray regions).

atomic coordinates of the $\beta2$ structure is obviously too small to induce a significant electronic inequivalence of dimers 1 and 2. On the other hand, all dimer-related states show a small asymmetry with respect to the 2× direction, i.e., parallel to the dimers. This asymmetry, induced by the symmetry break due to the third-layer As dimer, could possibly explain the apparent rotation of one dimer per unit cell seemingly observed with STM.[8] However, such a dimer twist was reported for the α phase, which we found to be symmetric with respect to both the atomic coordinates and the electronic wave functions. Difficulties to discriminate between the two two-dimer structures α and $\beta2$ by means of STM or effects of biasing[39] are possible explanations. The asymmetry of the empty states is much more pronounced than for the occupied states. The lowest unoccupied state $C1$, close to the conduction-band edge, is related to empty Ga dangling bonds located at threefold-coordinated second-layer Ga atoms (cf. Fig. 6). However, this state is nearly entirely localized at the Ga atoms on one side of the dimer block (close to the third-layer As dimer). The complementary state at the Ga atoms on the other side of the dimer block is about 0.2 eV higher in energy. $C2$ is an antibonding σ^* combination of in-plane p orbitals at the top-layer As dimers.

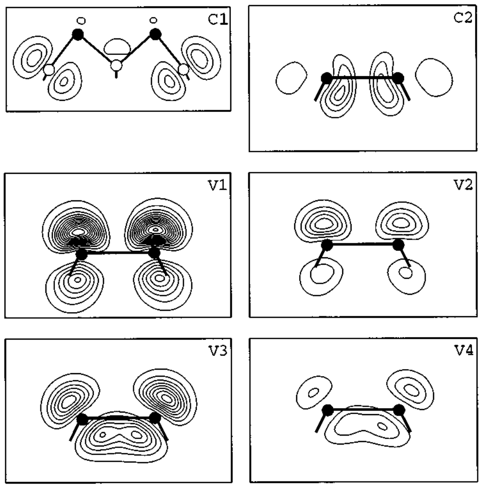

FIG. 6. Contour plots of the squared wave functions at K for surface localized states of the GaAs(001)$\beta2(2\times4)$ surface. The contour spacing is 10^{-3} e bohr^{-3}. All plots are drawn parallel to the surface normal. $C1$ is plotted along a plane parallel to the ×4 direction cutting through the bonds between first- and second-layer anions and through dimer 3 (cf. Fig. 1). $C2$, $V2$, and $V4$ are localized both at dimers 1 and 2 and have at both dimers nearly identical charge distributions. $V1$ and $V3$ are shown at dimer 3.

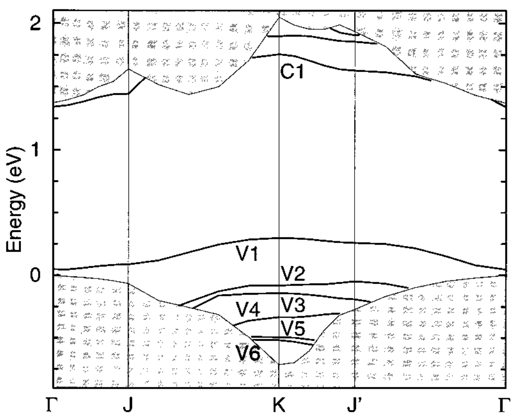

FIG. 7. Surface band structure (bound states) for GaAs(001)$\beta(2\times4)$ plotted over the projected bulk band structure (gray regions).

Although the three-dimer β model is no equilibrium phase of the GaAs(001)(2×4) surface, it has apparently been observed in a series of experiments. Therefore we have shown the surface band structure and the orbital character of states for the three-dimer model in Figs. 7 and 8, respectively. In the case of the GaAs(001)$\beta(2\times4)$ structure we find a small extension (0.3 eV at K) of the highest occupied state $V1$ into the region of the fundamental gap. As already observed for the α and $\beta2$ structures, the orbital character of that state is that of an antibonding π^* combination of p_z orbitals. It is localized at the middle dimer. $V2$ represents a σ bonding state between the topmost As dimer atoms and the fourfold-coordinated Ga atoms below. Very close in energy is $V3$, which arises from a π bonding of the middle dimer. The lower-lying states $V4$, $V5$, and $V6$ are the corresponding antibonding π^* and bonding π combinations localized at dimers 1 and 3. These two dimers are electronically equivalent. The energetical ordering of the valence states described above is in agreement with a theoretical simulation of STM images based on pseudopotentials.[40] In that work it was stressed that for a low bias only the middle dimer should be observable. The lowest unoccupied state $C1$ corresponds to empty Ga dangling bonds located at threefold-coordinated second-layer Ga atoms.

There are a number of features common to the electronic structure of all GaAs(001)(2×4) reconstructions discussed above. The highest occupied surface states are related to antibonding π^* combinations of p_z orbitals at the As dimers. The energetical positions of these states are slightly below ($\beta2$) or above (α and β) the bulk VBM. Their orbital character and energetical position are similar to the highest occupied surface state at the GaAs(110) surface.[41] Energeti-

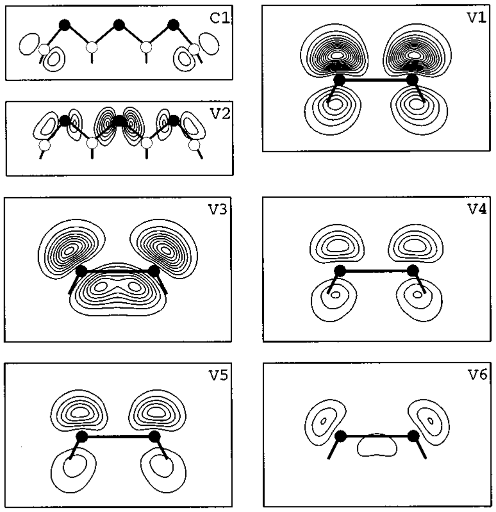

FIG. 8. Contour plots of the squared wave functions at K for surface localized states of the GaAs(001)$\beta(2\times4)$ surface. The contour spacing is $10^{-3}e$ bohr^{-3}. All plots are drawn parallel to the surface normal. $C1$ and $V2$ are plotted along a plane parallel to the $\times4$ direction cutting through the bonds between first-layer anions and second-layer cations. $V1$ and $V3$ are localized at the middle dimer. $V4$, $V5$, and $V6$ are localized at the electronically equivalent dimers 1 and 3.

TABLE II. Ionization energies (in eV) for the α, $\beta2$, and β reconstruction models of GaAs(001).

GaAs(110) (2×4)	α	$\beta2$	β
Present results	5.33	5.43	5.50
Experiment [a]	5.4	5.5	5.5

[a] Reference 20.

cally lower-lying bound surface states arise from the corresponding As-dimer π bonds and perturbed σ-like Ga-As back bonds. The lowest unoccupied surface states are related to Ga p orbitals, which is also in agreement with the findings for the GaAs(110) surface. We find these states slightly below the bulk CBM for all structures. That does not mean that these intrinsic surface states pin the Fermi level for n-type GaAs. The band structures presented here suffer 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 much more than empty bulk states towards higher energies.[42] Therefore we expect the unoccupied surface states to lie above the conduction-band edge. Neither the unoccupied nor the occupied surface states can account for the measured Fermi-level pinning.[18] We therefore believe that the defects observed at the GaAs(001) surface[19] are responsible for the pinning of the Fermi energy.

Our calculations lead to a slightly different picture of the As-dimer bonding than predicted in earlier heuristic studies. In these works (see, e.g., Refs. 16 and 18) each As dimer is supposed to accomodate six electrons, two in each dangling bond and two in the dimer bond itself. We find instead that the As dimers are bonded by σ and π combinations of the dehybridized As dangling bonds. A similar picture holds for the symmetric carbon dimers at the diamond(001) surface.[43] However, additionally, the antibonding π^* combinations are occupied for the As dimers, in contrast to the diamond surface. Whereas the π and π^* combinations (see, e.g., $V3$ and $V1$ in Fig. 6) lie close the bulk valence-band edge, the σ bonds are energetically degenerate with bulk bands. For the GaAs(001)$\beta2$ structure we find the σ-bond related states at 2.0 and 2.9 eV below the bulk VBM at K. Because of the problematic identification of resonant surface states in slab calculations we have not mapped the corresponding bands. They explain the experimental finding of a surface state at about 3 eV below the VBM.[21,22] The unoccupied σ^* combinations (see $C2$ in Fig. 6) are close to the CBM and represent a bound surface state in case of the $\beta2$ structure. ARPES (Refs. 21 and 22) has mapped some weakly dispersive dangling-bond-like surface states (S_1, S_2, S_3, and S_3') in the energy range 0.5–1.6 eV below the bulk VBM. This agrees with our findings of combinations of p_z orbitals ($V1$–$V4$) 0.3–0.8 eV below the VBM at K for the $\beta2$ structure. The small discrepancy in the energetical position could be due to different quasiparticle shifts of the VBM and surface localized states.[42] The extension of occupied surface states into the region of the fundamental bulk gap calculated for the α and β structures is certainly too large to be due to computational or experimental uncertainties or different quasiparticle shifts. Therefore, we think that the experimental results are best described by the calculated band structure of the $\beta2$ reconstruction.

The Coulomb potential obtained during the calculation allows one to determine the barrier experienced by an electron passing from the bulk to the vacuum region. The ionization energy corresponds to the difference between this potential barrier and the VBM. Our results for the ionization energies of the 2×4 reconstructions of GaAs(001) are given in Table II together with the experimental data available. We observe excellent agreement, in particular with respect to the trend observed with the As coverage. The transition from the $\beta2/\beta$ structure ($\Theta = 3/4$) to the α phase ($\Theta = 1/2$) is accompanied by a slight reduction of the ionization energy. This is caused by the reduced surface dipole between surface anions and cations. The measured reduction by 0.1 eV can be exactly reproduced for the $\beta2$-α transition, whereas the ionization energy of the three-dimer β structure is slightly higher. This is a further indication that the $\beta2$ structure rather than the β model corresponds to the actual surface geometry for an As coverage of $\Theta = 3/4$.

IV. SUMMARY

In conclusion, we have studied the atomic and electronic structures of the models used to describe the As-rich 2×4 reconstructions of the GaAs(001) surface by means of *ab initio* calculations. All geometries are characterized by As dimers and structural elements already known from the GaAs(110) surface. Threefold-coordinated nearly planar situated Ga atoms cause the dimer block to steepen. The As-As dimer length is remarkably constant for all models considered and amounts to 2.5 Å. The α structure represents the ground-state geometry for a relatively small range of the As chemical potential. It becomes unstable with respect to the $\beta2$ structure in more As-rich conditions. The three-dimer β

structure and a partial mixing of the substrate constituents in the uppermost layer studied for one example give rise to metastable structures that are higher in energy. Not only the geometries, but also the electronic structures of the models investigated show a series of common features. We observe As dimer bonding π and antibonding π^* combinations of p_z orbitals close to the bulk valence-band edge and empty Ga dangling bonds near the bulk CBM. The fundamental gap is free of states, at least in the $\beta2$ case. These features resemble the electronic structure of the GaAs(110) surface. The experimental findings available so far for the electronic structure of GaAs(001)(2×4) surfaces are best described with the $\beta2$ structure as the surface geometry for an As coverage of $\Theta = 3/4$.

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[1] H.H. Farrell and C.J. Palmstrøm, J. Vac. Sci. Technol. B **8**, 903 (1990).
[2] T. Hashizume, Q.K. Xue, J. Zhou, A. Ichimiya, and T. Sakurai, Phys. Rev. Lett. **73**, 2208 (1994).
[3] T. Hashizume, Q.K. Xue, A. Ichimiya, and T. Sakurai, Phys. Rev. B **51**, 4200 (1995).
[4] D.J. Chadi, J. Vac. Sci. Technol. A **5**, 834 (1987).
[5] J.E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993); Phys. Rev. B **50**, 2015 (1994).
[6] M.D. Pashley, K.W. Haberern, W. Friday, J.M. Woodall, and P.D. Kirchner, Phys. Rev. Lett. **60**, 2176 (1988).
[7] D.K. Biegelsen, R.D. Bringans, J.E. Northrup, and L.-E. Swartz, Phys. Rev. B **41**, 5701 (1990).
[8] L.D. Broekman, R.C.G. Leckey, J.D. Riley, A. Stampfl, B.F. Usher, and B.A. Sexton, Phys. Rev. B **51**, 17 795 (1995).
[9] T. Ohno, Phys. Rev. Lett. **70**, 631 (1993).
[10] S.A. Chambers, Surf. Sci. **261**, 48 (1992).
[11] H. Li and S.Y. Tong, Surf. Sci. **282**, 380 (1993).
[12] C. Xu, K.P. Caffey, J.S. Burnham, S.H. Goss, B.J. Garrison, and N. Winograd, Phys. Rev. B **45**, 6776 (1992).
[13] G.-X. Qian, R.M. Martin, and D.J. Chadi, Phys. Rev. B **38**, 7649 (1988); Phys. Rev. Lett. **60**, 1962 (1988).
[14] G.P. Srivastava and S.J. Jenkins, Phys. Rev. B **53**, 12 589 (1996).
[15] K. Shiraishi and T. Ito, J. Cryst. Growth **150**, 158 (1995).
[16] M.D. Pashley, Phys. Rev. B **40**, 10 481 (1989).
[17] J. Massies, P. Etienne, F. Dezaly, and N.T. Linh, Surf. Sci. **99**, 121 (1980).
[18] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer-Verlag, Berlin, 1995), and references therein.
[19] M.D. Pashley and K.W. Haberern, Phys. Rev. Lett. **67**, 2679 (1991).
[20] H. Tsuda and T. Mizutani, Appl. Phys. Lett. **60**, 1570 (1992).
[21] P.K. Larsen and J.D. van der Veen, J. Phys. C **15**, L431 (1982).
[22] P.K. Larsen, J.F. van der Veen, A. Mazur, J. Pollmann, J.H. Neave, and B.A. Joyce, Phys. Rev. B **26**, 3222 (1982).
[23] J. Ihm, D.J. Chadi, and J.D. Joannopoulos, Phys. Rev. B **27**, 5119 (1983).
[24] Y.-C. Chang and D.E. Aspnes, J. Vac. Sci. Technol. B **8**, 896 (1990).
[25] R. Rincón, R. Saiz-Pardo, R. Pérez, and F. Flores, in *Proceedings 4th International Conference on the Formation of Semiconductor Interfaces (ICFS1-4),* edited by B. Lengeler, H. Lüth, W. Mönch, and J. Pollmann (World Scientific, Singapore, 1994), p. 293.
[26] J. Falta, R.M. Tromp, M. Copel, G.D. Pettit, and P.D. Kirchner, Phys. Rev. Lett. **69**, 3068 (1992).
[27] K. Shiraishi, J. Phys. Soc. Jpn. **59**, 3455 (1990).
[28] R. Stumpf and M. Scheffler, Comput. Phys. Commun. **79**, 447 (1994).
[29] X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).
[30] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[31] R.A. Evarestov and V.P. Smirnov, Phys. Status Solidi B **119**, 9 (1983).
[32] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[33] W.G. Schmidt, F. Bechstedt, and G.P. Srivastava, Phys. Rev. B **52**, 2001 (1995).
[34] N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon, New York, 1984), p. 643.
[35] *Table of Periodic Properties of the Elements* (Sargent-Welch Scientific Company, Skokie, IL, 1980).
[36] *Handbook of Chemistry and Physics*, 65th ed., edited by R.C. Weast (Chemical Rubber Company, Boca Raton, FL, 1984).
[37] A.R. Avery, C.M. Goringe, D.M. Holmes, J.L. Sudijono, and T.S. Jones, Phys. Rev. Lett. **76**, 3344 (1996).
[38] W.G. Schmidt and F. Bechstedt, Surf. Sci. Lett. **360**, L473 (1996).
[39] P. Badziag, W.S. Verwoerd, and M.A. van Hove, Phys. Rev. B **43**, 2058 (1991).
[40] J.M. Bass and C.C. Matthai, Phys. Rev. B **50**, 11 212 (1994).
[41] J.L.A. Alves, J. Hebenstreit, and M. Scheffler, Phys. Rev. B **44**, 6188 (1991).
[42] F. Bechstedt and R. Del Sole, Solid State Commun. **74**, 41 (1990).
[43] C. Kress, M. Fiedler, W.G. Schmidt, and F. Bechstedt, Phys. Rev. B **50**, 17 697 (1994).