Antimony-stabilized GaAs(001)(2×4) reconstructions

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Structural and electronic properties of the Sb-stabilized GaAs(001)(2×4) reconstructions are studied by means of *first-principles* pseudopotential calculations. Six structural models with Sb coverages of $\Theta=\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$ are considered. The atomic geometries are optimized by means of total-energy calculations. Models with one or two Sb dimers in the first atomic layer describe the stable surface depending on the chemical potentials of the surface constituents. The model widely accepted so far, containing three dimers in the outermost layer, is unfavorable from the energetical point of view. The lengths of the Sb dimers are about 2.9 Å, in close agreement with recent x-ray standing-wave measurements. The surface electronic structures are similar to those of As-rich GaAs(001) surfaces and dominated by filled Sb-dimer states and empty Ga dangling bonds close to the GaAs valence- and conduction-band edges, respectively. [S0163-1829(97)04919-9]

I. INTRODUCTION

The behavior of group-V elements on III-V compound semiconductor surfaces is technologically important and also interesting from a surface science point of view.[1] In particular, the understanding of the adsorption of these elements on (001) faces is an essential step towards the understanding of the initial stages of growth and III-V heteroepitaxy.[2] The same holds for the initial stages of the Schottky barrier formation in the case of the deposition of semimetals. A prototypical example is the adsorption of Sb on GaAs(001), which leads to the formation of an exceptionally abrupt interface.[2,3] Moreover, Sb seems to be useful as a surfactant for metal growth on GaAs(001).[4,5]

The structural, electronic, and dynamical properties of Sb/GaAs(110) interfaces have been studied in much detail (see, e.g., Ref. 1). Sb atoms of the first monolayer form zigzag chains bonded to both As and Ga atoms on the GaAs(110) surface. In contrast, Sb adsorption on GaAs(001) surfaces has only recently become the subject of experimental and theoretical investigations. Surface details, such as the atomic arrangement and electronic states, are not well understood. Sb deposition on As-terminated GaAs(001) surfaces at room temperature and subsequent annealing lead to a variety of reconstructions.[2,6,7] Among those the 2×4 surface is the most interesting one. It shows a very clear and streaky reflection high-energy electron diffraction (RHEED) pattern. Soft x-ray photoemission spectroscopy (SXPS), Auger electron spectroscopy, RHEED, and scanning tunneling microscopy (STM) studies indicate a stabilization of the 2×4 surface by Sb dimers.[2,6–9] The dimer reconstruction model for the Sb-stabilized GaAs(001)(2×4) surface has also been supported by x-ray standing-wave experiments[10] and reflectance anisotropy spectroscopy (RAS).[11]

Ab initio total-energy studies[11,12] of the 2×4 translational symmetry of the Sb-terminated GaAs(001) face give additional support to the dimer reconstruction model. However, the actual reconstruction model, the geometrical details of this model, and the resulting electronic structure are not very clear. This is in contrast to the As-rich GaAs(001)(2×4) reconstructions. In the latter case α, β, and γ phases have been found experimentally and identified[13–16] with a two-As-dimer model (α), a three-As-dimer model with either three dimers in the top layer (β), or two dimers in the top layer and an additional As dimer in the third layer ($\beta2$), or a mixture of different surface phases (γ). The phase diagram of these reconstructions indicates a stabilization of the α phase under less As-rich conditions, whereas the $\beta2$ structure is observed for higher values of the As chemical potential.

In this work we present results of converged *first-principles* calculations for six structural models for different Sb stoichiometries derived from the favorable structures for the As-stabilized surface, but supplemented by one-dimer geometries. We provide a detailed analysis of the atomic structures and discuss their stability versus the chemical potentials of the surface constituents. The structural data obtained are compared with the available experimental information. Based on the relaxed geometries, we analyze the surface states and the ionization energies of the phases that are favorable from the energetical point of view.

II. NUMERICAL DETAILS

We model the overlayer system by a repeated slab geometry with an artificial periodicity along the surface normal. One unit cell includes a material slab with nominally eight atomic GaAs(100)(2×4) layers and a vacuum region equivalent in thickness. The Ga-terminated surface of the slab is saturated with fractionally charged hydrogen atoms.[17] The two bottom layers on this side of the slab are kept frozen, whereas all other atoms are allowed to relax. The As-terminated slab surface is modified in order to realize the specific surface geometry and stoichiometry. We account for the electric field caused by the two inequivalent surfaces of the slab by applying a dipole correction[18] to the self-consistently calculated electrostatic potential.

Our calculations are based on the density-functional theory in the local-density approximation and are performed using fully separable norm-conserving pseudopotentials.[19] Single-particle orbitals are expanded into plane waves up to a kinetic energy cutoff of 15 Ry. The exchange-correlation potential of Ceperley and Alder[20] is chosen to describe the

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TABLE I. Geometrical parameters (in Å) of six models for relaxed Sb/GaAs(001)(2×4) structures according to Fig. 1. Other theoretical results (Ref. 12) for the δ_1 structure are given in parentheses.

Sb/GaAs(100)	β_3	α_2	$\beta2_2$	$\beta2_3$	δ_1	δ_2
$\Delta_{a1,x}$	2.86	2.86	2.86	2.86	2.87(2.79)	2.87
$\Delta_{a2,x}$	2.86	2.86				
$\Delta_{b1,x}$	3.73	3.87	3.72	3.73	3.75	3.74
$\Delta_{b2,x}$	3.63	3.71	3.64	3.66	3.75	3.75
$\Delta_{b3,x}$		3.62			3.89	3.89
$\Delta_{b4,x}$		3.72				
$\Delta_{c,x}$			2.52	2.87	2.53(2.39)	2.88
$\Delta_{d,x}$			3.68	3.76	3.69	3.76
$\Delta_{a,y}$	3.91	4.01	3.95	3.95		
$\Delta_{b,y}$		2.45			2.44(2.48)	2.43
$d_{ab,y}$	1.47	1.57	1.46	1.45	1.88	1.86
$d_{ab',y}$		1.81	1.48	1.47	1.62	1.61
$d_{ac,y}$			5.94	5.93	9.43	9.43
$\Delta_{a,\perp}$	0.09	0.09				
$\Delta_{b12,\perp}$	0.19	0.23	0.26	0.26	0.14	0.14
$\Delta_{b23,\perp}$		0.15			0.29(0.25)	0.29
$\Delta_{b34,\perp}$		0.17				
$d_{ab,\perp}$	1.68	1.64	1.74	1.74	1.81(1.52)	1.82

many-body electron-electron interaction. The **k**-space integration over the Brillouin zone (BZ) is replaced by a sum over a set of special points,[21] corresponding to eight points in the full two-dimensional surface BZ. The minimum of the total energy with respect to both the electronic and atomic degrees of freedom is found by means of a molecular-dynamical approach.[18,22] The atoms are assumed to be in their fully relaxed positions when the forces acting on the ions are smaller than 25 meV/Å. We perform the calculations with the theoretical equilibrium lattice constant of 5.56 Å for bulk GaAs, which is 1.7% smaller than the experimental value. This approach and the numerical parameters have proven successful in determining precisely the structural, electronic, and dynamical properties of the Sb/GaAs(110) interface.[1] The study presented here is on the same footing as recent investigations of As-rich GaAs(001)(2×4) reconstructions,[16] allowing meaningful comparisons.

III. RESULTS AND DISCUSSION

A. Reconstruction models

Taking the chemical similarity of As and Sb into account, similar reconstructions are expected for As-rich and Sb-stabilized GaAs(001) surfaces. Three GaAs(001)(2×4) structures, α, β, and $\beta2$, have therefore been used as a starting point to derive models for the Sb-terminated GaAs(001) surface. In order to denote the adsorption geometries we modify the notation of Northrup and Froyen[15] for the clean surface. Subscripts $n=1$, 2, or 3 indicate the Sb coverage $\Theta=n/4$. Reconstruction models with only one anion dimer in the top layer are denoted by δ.

The β_3 adsorption structure results from the replacement of the three first-layer As dimers of the GaAs(001)β structure by Sb dimers (cf. Fig. 1), giving rise to an Sb coverage of $\Theta=\frac{3}{4}$. Accordingly, we obtain the α_2 adsorption model by an antimony substitution of the two As dimers of the GaAs(001)α phase. Two more models, $\beta2_2$ and $\beta2_3$, are derived from the GaAs(001)$\beta2(2\times4)$ reconstruction by replacing either the uppermost or all As dimers by Sb dimers. Consequently, the Sb coverage amounts to $\Theta=\frac{1}{2}$ in the case of the α_2 and $\beta2_2$ structures and $\Theta=\frac{3}{4}$ for the $\beta2_3$ adsorption geometry. The β_3 model was originally proposed by Maeda and co-workers[2] to explain their SXPS data and RHEED pattern for the Sb-induced 2×4 reconstruction of the GaAs(001) surface. A comparison of tight-binding results for surface optical properties of the β_3, α_2, $\beta2_2$, and $\beta2_3$ adsorption geometries (denoted as models I–IV) with RAS spectra favors the two-dimer α_2 structure.[11] On the other hand, from recent STM studies, Moriarty *et al.*[6] have suggested a surface reconstruction model with only one single Sb dimer, which has no counterpart in the clean surface case. Therefore we investigate also the δ_1 and δ_2 structures shown in Fig. 1. We mention that all structures considered here may satisfy the electron counting rule.[23] This requires, however, the formation of Ga dimers in the second atomic layer for the α and δ structures.

B. Atomic geometries

In order to determine the ground-state geometry of the adsorption models discussed above we relaxed a series of different structures containing buckled and twisted Sb dimers, missing As or Ga pairs, and sometimes Ga dimers in the second atomic layer. The minimum-energy geometries are presented in Fig. 1. The structural parameters indicated in Fig. 1 are listed in Table I.

All models are characterized by the formation of strong Sb-Sb dimers. Independent of the specific reconstruction model and the surface stoichiometry we find a nearly constant dimer length. It amounts in the first atomic layer to $\Delta_{a1,x}$, $\Delta_{a2,x}=2.86-2.87$ Å and to $\Delta_{c,x}=2.87-2.88$ Å in the third layer. These values are slightly larger than the Sb-Sb bond length of 2.81 Å calculated for the monolayer Sb-covered GaAs(110) surface[1] and larger than the sum of the Sb covalent radii of 2.80 Å.[24] The Sb dimers are symmetric in the case of the β_3 and α_2 structures, while we find a very small buckling accompanied by a nearly vanishing dimer twisting for the adsorption geometries, where a third-layer dimer breaks the symmetry. The largest buckling of 0.05 Å occurs for the third-layer dimer of the $\beta2_3$ structure. The nearly symmetric nature of the surface Sb dimers as well as their bond lengths are in agreement with the x-ray standing-wave (XSW) work. Sugiyama *et al.*[10] estimated a dimer length of 2.95 ± 0.06 Å. Another *ab initio* calculation[12] performed for the δ_1 structure determined a Sb dimer bond length of 2.79 Å. Also the other structural parameters given in Ref. 12 deviate somewhat from our findings (cf. Table I). These discrepancies may be due to the small number of GaAs layers in the material slab and the Γ-point summation used by Srivastava and Jenkins.

The near conservation of geometrical quantities independent of the specific reconstruction model holds especially for the lateral distances, since they are largely determined by the GaAs substrate. Stronger variations occur for vertical distances. One pronounced example concerns the minimum dis-

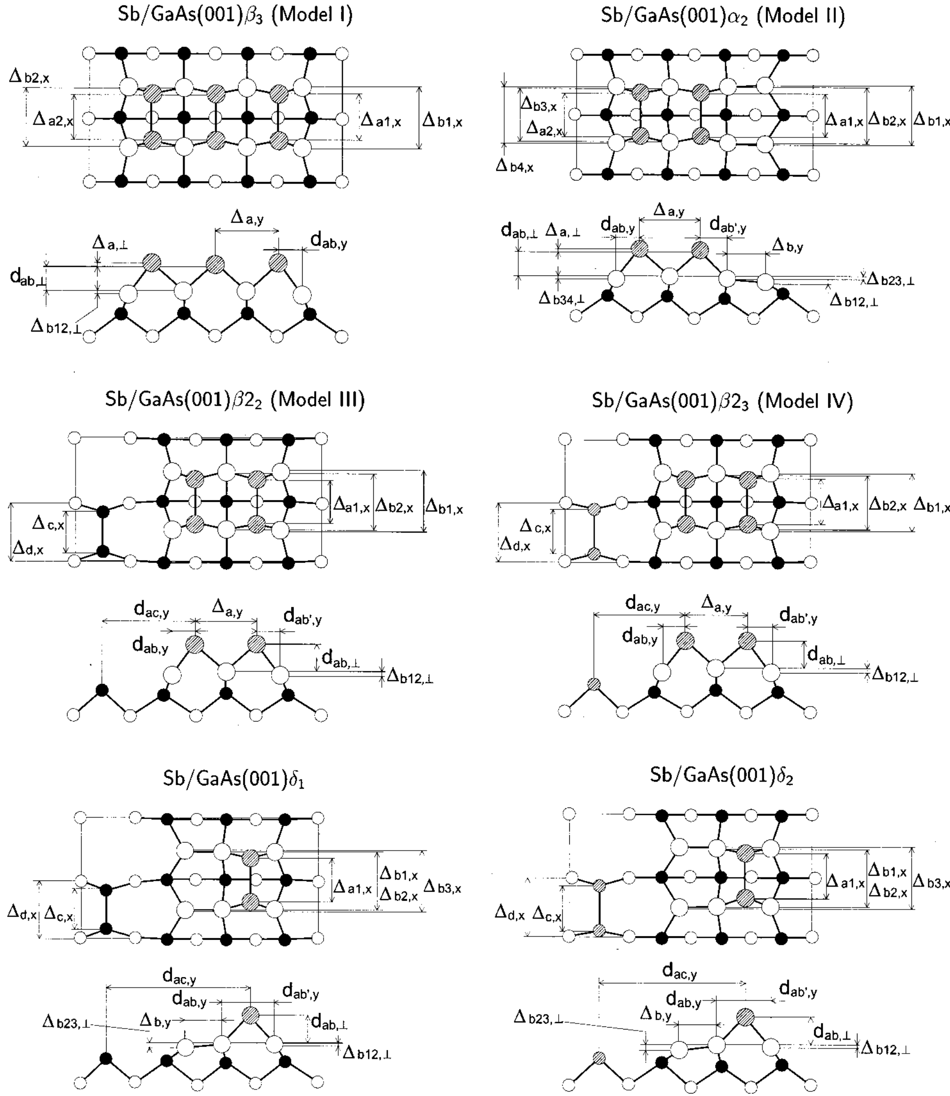

FIG. 1. Top and side views of the six Sb/GaAs(001)(2×4) structures under consideration. In parentheses we give the notation of the adsorption geometries according to Ref. 11. Large (small) circles indicate top- and second- (third- and fourth-) layer atoms. Substrate anions (substrate cations, antimony atoms) are denoted by full (empty, shaded) symbols. Characteristic lateral and vertical distances are indicated. The x and y directions are along $[1\bar{1}0]$ and [110], respectively.

tance between the first-layer Sb dimers and the second-layer Ga lattice plane, $d_{ab,\perp}$. We observe a variation between 1.64 and 1.82 Å. From the covalent radii, $r_{\rm Ga}+r_{\rm Sb}=2.62$ Å,[24] and bulk positions we expect a smaller value of $d_{ab,\perp}=1.51$ Å. However, the threefold-coordinated second-layer Ga atoms bonded to Sb dimer atoms prefer a nearly planar, sp^2-like bonding situation. This leads to an upward movement of the Sb dimers. A similar relaxation known as steepening has also been observed for As-rich GaAs(001) surfaces.[16,25] This effect is most pronounced for isolated Sb dimers in the top layer, i.e., in the case of the δ structures. Here, we end up with values $d_{ab,\perp}=1.81-1.82$ Å, very close to the value 1.81 ± 0.02 Å measured by XSW.[10] This is a strong indication for the validity of one-top-dimer models. The other existing theoretical value $d_{ab,\perp}=1.52$ Å (Ref. 12) fails the criterion of increased substrate-overlayer distances.

Further interesting quantities are the lateral Ga-Ga distances. There are Ga atoms in the second layer with none, one, or two Sb neighbors in the top layer. We observe a dimerization of the originally twofold- and threefold-coordinated Ga atoms of the δ_1, δ_2, and α_2 structures. The corresponding lateral distances $\Delta_{b,y}$ vary between 2.43 and 2.45 Å. They are shorter than the sum of the Ga covalent radii of 2.52 Å (Ref. 24) and, hence, indicate indeed a strong dimerization. The coexistence of Sb and Ga dimers at the Sb-stabilized GaAs(2×4) surface has been concluded from a recent RAS study.[11] Because of the fourfold or threefold coordination of the involved atoms these Ga dimers are buckled. The buckling $\Delta_{b23,\perp}=0.15$ Å is smaller in the case of the α_2 reconstruction compared with the value $\Delta_{b23,\perp}=0.29$ Å for the structures δ_1 and δ_2. The vertical displacement can be understood from the tendency of the threefold-coordinated Ga atoms to form nearly planar, sp^2-like bonds, whereas the fourfold-coordinated Ga atoms keep their sp^3 hybridization. Consequently, the latter move upward.

C. Energetics

All six reconstruction models considered in Fig. 1 give rise to local minima on the Born-Oppenheimer total-energy face. On the other hand, the structures represent different surface stoichiometries. The ground state of the surface, i.e., the favorable structure, therefore depends on the deposition conditions during the surface preparation. The stability of a certain structure in the equilibrium may be determined from

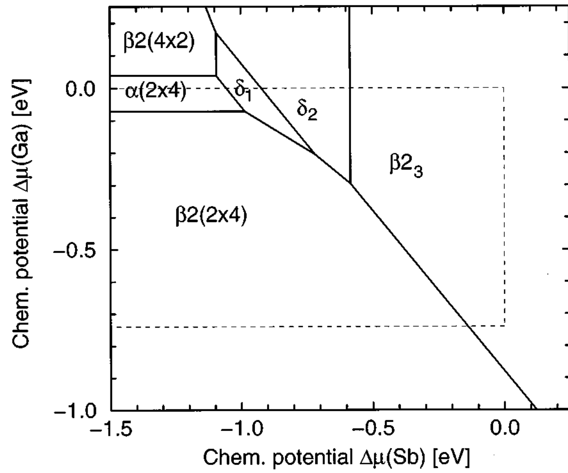

FIG. 2. Phase diagram of the Sb-stabilized and As-rich GaAs(001)(2×4) reconstructions as well as the Ga-terminated GaAs(001)$\beta 2(4\times 2)$ surface vs the Ga and Sb chemical potentials. Dashed lines indicate the approximate range of thermodynamically allowed values of $\Delta\mu(i)$.

the surface free energy and the chemical potentials $\mu(i)$ of the surface constituents $i=$Ga, As, and Sb. Thereby, the chemical potentials of Ga and As depend on each other: the surface is in equilibrium with the GaAs bulk. Pairs of Ga and As atoms can be exchanged with the bulk. Consequently, it holds that

$$\mu(\mathrm{GaAs})_{\mathrm{bulk}}=\mu(\mathrm{Ga})+\mu(\mathrm{As}), \tag{1}$$

where $\mu(\mathrm{GaAs})_{\mathrm{bulk}}$ is the energy per unit cell of bulk GaAs. Therefore the surface formation energy is a function of only two chemical potentials $\mu(i)$. We use μ(Ga) and μ(Sb). The Sb chemical potential is assumed to be independent of the values for Ga or As. The experimental conditions that determine μ(Ga) will, of course, also affect μ(Sb). Upper limits of the chemical potentials are given by those of the bulk elements,[26] $\mu(\mathrm{Ga})_{\mathrm{bulk}}$ and $\mu(\mathrm{Sb})_{\mathrm{bulk}}$. The lower limit of μ(Ga) can be determined from

$$\mu(\mathrm{Ga})+\mu(\mathrm{As})=\mu(\mathrm{Ga})_{\mathrm{bulk}}+\mu(\mathrm{As})_{\mathrm{bulk}}-\Delta H_f(\mathrm{GaAs}). \tag{2}$$

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

$$-\Delta H_f(\mathrm{GaAs})\leq\mu(\mathrm{Ga})-\mu(\mathrm{Ga})_{\mathrm{bulk}}=:\Delta\mu(\mathrm{Ga})\leq 0. \tag{3}$$

For the heat of formation ΔH_f(GaAs) we use the experimental value of 0.74 eV.[27] There are, however, also other data available: $\Delta H_f(\mathrm{GaAs})=0.84$ eV and $\Delta H_f(\mathrm{GaAs})=0.94$ eV. [28] We calculate a value of 0.77 eV. This gives a rough estimate for the accuracy of the calculated phase diagram in Fig. 2. The lower limit of the Sb chemical potential is in principle given by the extreme situation, where no antimony is available in the recipient. However, the physically interesting range of μ(Sb) is determined by the stability of the Sb-covered versus the clean GaAs(001) surface.

The equilibrium phase of the Sb/GaAs(001)(2×4) reconstruction is given by the surface that, for given values of the Ga and Sb chemical potentials, minimizes the function[26]

$$G_{\mathrm{surf}}(\{n_i\})-\sum_i \mu(i)n_i\approx E_{\mathrm{surf}}(\{n_i\})-\sum_i \mu(i)n_i. \tag{4}$$

$G_{\mathrm{surf}}(\{n_i\})$ is the surface free energy as a function of the surface stoichiometry, which is approximated by the total surface energy $E_{\mathrm{surf}}(\{n_i\})$ at zero temperature. The n_i are the number of atoms of species $i=$Ga, As, or Sb. The first term in Eq. (4) contains the energy gain due to the displacements of the surface atoms into the equilibrium positions. The second term accounts for energy differences due to different surface stoichiometries. The resulting phase diagram in dependence on the chemical potentials of surface Ga and Sb atoms is shown in Fig. 2. In this phase diagram we compare the energies of the Sb-stabilized GaAs(001)(2×4) reconstructions with those of the As-rich GaAs(001)(2×4) surface phases[16] and the Ga-terminated GaAs(001)$\beta 2(4\times 2)$ surface.

The energies of the β_3 and α_2 structures can directly be compared with the ones of models $\beta 2_3$ and δ_2, respectively, since they differ simply by one GaAs pair. The total energies of the $\beta 2_3$ and δ_2 structures are 0.03 and 0.02 eV per (1×1) surface unit cell lower than that of the respective β_3 and α_2 structures. These energetical differences are slightly smaller than the one found between the β and $\beta 2$ reconstruction of the clean GaAs(001)(2×4) surface.[15,16] Consequently, the two structures β_3 and α_2 do not appear in Fig. 2. Also the $\beta 2_2$ adsorption geometry does not occur in the calculated phase diagram. Considering the limited accuracy of our calculations we can, however, not exclude this structure to be stable in a very small range between the $\beta 2_3$ adsorption geometry and the As-rich $\beta 2(2\times 4)$ reconstruction of the clean GaAs surface.

From the three remaining structures we find the $\beta 2_3$ model to be stable in the extreme limit, where the Sb chemical potential nearly equals the bulk value. The $\delta_{1/2}$ structures with one top Sb dimer become more favorable for lower values of μ(Sb). This holds, however, only for Ga-rich conditions. The experimentally observed Sb/GaAs(001)(2×4) reconstruction should occur in this region of the phase diagram, since a well ordered Sb-terminated GaAs(001)(2×4) surface is formed at temperatures much higher than the clean, As-terminated surface.[2,8,9] The calculated phase diagram in conjunction with the information available about the preparation conditions therefore indicates that the δ_1 or δ_2 structure corresponds to the actual observed adsorption geometry. This finding agrees with recent RAS measurements,[11] which indicate a coexistence of Ga and Sb dimers at the surface and STM images,[6] which suggest the termination of the GaAs(001) surface by single Sb dimers in the top layer. However, under more Sb-rich conditions the $\beta 2_3$ structures with two Sb dimers in the top atomic layer may appear. It corresponds to the highest Sb coverage under consideration ($\Theta=\frac{3}{4}$). A rather interesting result of the phase diagram in Fig. 2 concerns the near coexistence of the three phases $\beta 2_3$, δ_1, and δ_2 for intermediate values of the

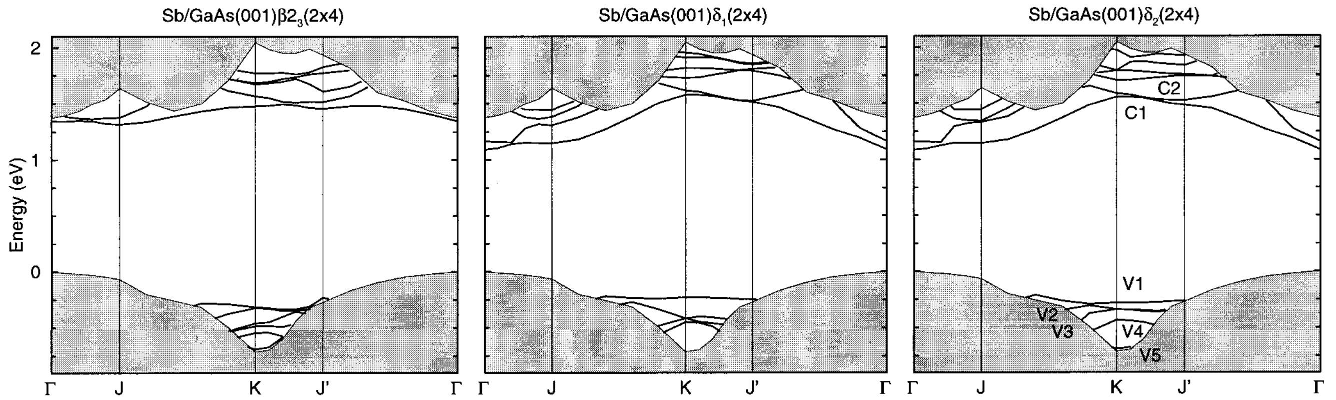

FIG. 3. Surface band structure (bound states) for the energetically favored $\beta 2_3$, δ_1, and δ_2 models of the Sb/GaAs(001)(2×4) surface. The projected GaAs bulk band structure is indicated by gray regions.

chemical potentials. This result may explain the different experimental findings[2,6,7,10,11] concerning the number of Sb dimers per surface unit cell.

From Fig. 2 the question arises why structures with only one Sb dimer in the top layer are energetically stable in contrast to the As-rich GaAs(001) surface, where (2×4) unit cells contain either two or three As dimers in the top layer.[14,29,30] One reason could be the steric repulsion of the Sb dimers. The covalent radii of Sb and As are $r_{\mathrm{Sb}}=1.36$ Å and $r_{\mathrm{As}}=1.18$ Å.[24] This leads to approximately a 0.1–0.2-Å larger dimer-dimer distance $\Delta_{a,y}$ compared to the As-terminated surface.[16]

D. Electronic properties

In Fig. 3 we show the bands of the bound surface states in the energy region of the fundamental gap for the energetically favored Sb-stabilized GaAs(001)(2×4) surface structures $\beta 2_3$, δ_1, and δ_2. The band structures are rather similar to those calculated for clean GaAs(001)(2×4) surfaces.[16] This is due to the occurrence of the same reconstruction elements: anion dimers in the first and third atomic layers and cation dimers in the second atomic layer in the case of the δ_1 and δ_2 structures. The midgap region is essentially free of surface states. A series of occupied anion-related bands occurs slightly below the bulk valence-band maximum (VBM). Empty, essentially Ga-related, surface bands are observed close to the bulk conduction-band edges. Their energetical position depends strongly on the coordination of the Ga atoms involved.

In the case of the two-Sb-dimer structure $\beta 2_3$ the band structure in Fig. 3 is very similar to that calculated for the $\beta 2$ reconstruction of the As-rich surface. In particular the positions of the highest occupied bound surface states are nearly identical. This is surprising if one considers the different orbital energies of Sb and As valence electrons: the p orbital energy of Sb is about 0.8 eV higher than that of As.[31] However, a near compensation of two opposite effects occurs. The As dimer bond length at the clean surface is about 2.5 Å (Ref. 16) much shorter than the Sb dimer bond length of about 2.9 Å at the Sb-stabilized face. Consequently, the $pp\pi$ interaction is smaller and the π^* levels of As and Sb dimers have similar energies.

The unoccupied surface states extend slightly into the region of the fundamental gap for the one-Sb-dimer structures δ_1 and δ_2. This shift with respect to the unoccupied bands of the $\beta 2_3$ structure may be related to the dimerization of the second-layer Ga atoms, which lowers the energy of the Ga states. The effect is, however, weakened by the trend of rehybridization $sp^3 \rightarrow sp^2 + p_z$. A similar observation has been made for the α and β phases of the As-rich GaAs(001)

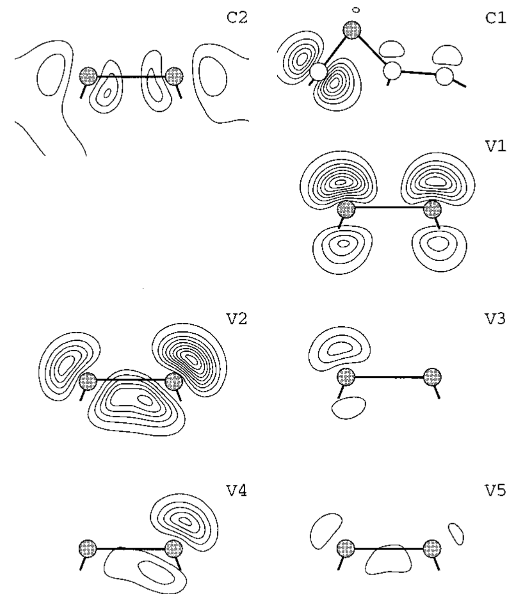

FIG. 4. Contour plots of the squared wave functions at K for localized states of the δ_2 structure of the Sb/GaAs(001)(2×4) surface. The contour spacing is $10^{-3} e/\mathrm{bohr}$. All plots are drawn parallel to the surface normal. $C1$ is plotted along a plane parallel to the ×4 direction cutting through the bonds between first- and second-layer anions and through the third-layer Sb dimer. $C2$, $V3$, $V4$, and $V5$ are localized at the top-layer Sb dimers. $V1$ and $V2$ are localized at the third-layer Sb dimer.

surface.[16] The position and dispersion of the occupied states is similar to those of the $\beta2_3$ structure. Since one of the δ structures probably corresponds to the Sb-induced (2×4) reconstruction observed in most experiments, we will discuss the electronic structure of this adsorption configuration in more detail.

The orbital character of several bound surface states is shown in Fig. 4 for the δ_2 structure. The highest occupied surface state, $V1$, 0.23 eV below VBM at K, corresponds to an antibonding π^* combination of the p_z orbitals localized at the third-layer Sb dimer. Only about 0.1 eV lower in energy we find the corresponding bonding π combination $V2$. Thus the splitting between π and π^* states is less than half the value calculated for the As dimers at the As-rich GaAs(001) surface.[16] It is interesting to note that the asymmetry of the Sb dimer states is somewhat more pronounced than found for the As-rich GaAs(001) surface. This becomes even more obvious in the case of the bound states $V3$ and $V4$, which correspond to dangling p_z orbitals at the top dimers. They are, however, only weakly localized. Even weaker is the surface localization of $V5$, which is nearly degenerate with bulk bands and corresponds to a π bonding state at the top Sb dimer. The lowest unoccupied surface state, $C1$, is related to an empty Ga dangling bond localized at the threefold coordinated Ga atom close to the third-layer Sb dimer. The complementary state at the Ga atom on the opposite side of the top Sb dimer is about 0.25 eV higher in energy. $C2$ is partially an antibonding σ^* combination of in-plane p orbitals at the top Sb dimer.

Our results for the orbital character of surface states are in agreement with a recent theoretical study on the δ_1 structure.[12] However, in contrast to the present study, Srivastava and Jenkins predict a surface band gap much smaller than that of bulk GaAs. We calculate a shrinkage of about 0.2 eV only. This discrepancy may be due to the structural differences, most probably caused by the thin slab and the small basis set used in Ref. 12. Very recently angle-resolved photoelectron spectroscopy experiments were performed on Sb/GaAs(001)(2×4) surfaces.[7] Two occupied bands have been observed for $\mathbf{k}$ vectors along the ΓJ and $\Gamma J'$ directions. The dispersion of these bands with 0.5 eV is rather weak. The bands are about 1.5 and 3 eV below the VBM. Therefore, they represent surface resonances and have not been mapped in the band structures presented here. At 1.5 eV below the bulk valence edge we find states related to pronounced σ bonds between the top-layer Sb dimer and the second-layer Ga atoms.

The electrostatic potential obtained during the self-consistent solution of the Kohn-Sham equations in our calculation allows one 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 valence-band maximum. For the As-rich GaAs(001)$\beta2(2\times4)$ surface we have calculated a value $I=5.43$ eV (Ref. 16) close to the measured ionization energy of $I=5.5$ eV.[32] For the Sb-covered surface we find a reduction ΔI with respect to the value for the clean surface. The corresponding values are $\Delta I=0.22$ and 0.26 eV for structures $\beta2_2$ and $\beta2_3$, respectively, and $\Delta I=0.42$ and 0.45 eV for the δ_1 and δ_2 models. These values indicate that the change of the ionization energy is essentially a function of the number N of Sb dimers in the top surface layer. It holds approximately $\Delta I=N(1-0.42N)0.75$ eV. In the case of the two-Sb-dimer structures $\beta2_{2/3}$ the reduction of I is due to the replacement of As by less electronegative Sb atoms.[24] The mechanism is similar to that discussed for alkali adsorption on GaAs surfaces.[33] An even larger reduction ΔI occurs for the one-Sb-dimer structures $\delta_{1/2}$. In these cases the smaller number of surface anions, compared to the As-rich surface, reduces additionally the ionization energy. On the other hand, the variation of I due to the exchange of an As dimer by an Sb dimer in the third layer is practically vanishing. The ionization energies for $\beta2$ and δ structures differ by 0.2 eV. Therefore, measurements of this quantity could give additional support for a specific adsorption configuration.

IV. SUMMARY

In conclusion, we have studied the energetics and the atomic and electronic structure of six different models for the Sb-stabilized GaAs(001)(2×4) surface by means of *ab initio* calculations. Structures already known from the clean surface have been modified by an As-Sb exchange. In addition, also surface geometries with only one Sb dimer in the first atomic layer have been considered. The minimum energy surface structure depends on the chemical potentials of the atomic species and, hence, on the surface preparation conditions. Three Sb dimers in the first atomic layer of the 2×4 unit cell are unstable, even under Sb-rich preparation conditions. In contrast to As-rich (2×4) reconstructions we find both one- and two-Sb-dimer structures to be stable. The calculated phase diagram in conjunction with the experimental preparation conditions indicates, however, that the structures most probably observed contain only one Sb dimer in the top layer. These one-Sb-dimer structures fit also best the existing XSW, STM, and RAS experiments. However, from the theoretical point of view the existence of a two-Sb-dimer structure with one additional Sb dimer in the third layer cannot be excluded, especially for Sb-rich conditions. All favorable structures are characterized by rather identical reconstruction elements. The Sb-dimer bond length is about 2.9 Å, in accordance with the measured value. The resulting electronic structures are rather similar compared to those calculated for As-rich GaAs(001)(2×4) surfaces. The fundamental gap is essentially free of surface states. The occupied surface bands are related to π bonding and π^* antibonding combinations of anion dimer orbitals. The empty bound surface states are mainly derived from Ga dangling bonds and σ^* antibonding anion dimer states. The Sb coverage reduces the ionization energy with respect to the As-rich surface for all structures investigated. The amount of reduction, however, depends on the actual surface stoichiometry, in particular on the number of Sb dimers in the top atomic layer.

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