(2×4) GaP(001) surface: Atomic structure and optical anisotropy

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We have investigated the microscopic structure and optical anisotropy of (2×4) reconstructed GaP(001) surfaces. Optical and electron spectroscopy from GaP(001) surfaces prepared in ultrahigh-vacuum conditions were combined with *first-principles* calculations of the energetics and reflectance anisotropy. Symmetry, composition and surface optical anisotropy were characterized by low-energy electron diffraction, Auger electron spectroscopy, photoemission spectroscopy and reflectance anisotropy spectroscopy. In contrast to most earlier reports, we find that the stable Ga-rich surface corresponds to a (2×4) reconstruction. No (4×2) reconstruction could be observed, independent of the preparation method. Depending on the Ga coverage, however, two distinct line shapes in the reflection anisotropy spectra occur, indicating the existence of at least two different surface phases with (2×4) periodicity. This agrees with our total-energy calculations: Four (2×4) structural models may be stable depending on the chemical potentials of the surface constituents. All considered (4×2) structures, however, are unstable. Based on the comparison between calculated reflectance anisotropy spectra and measured data we suggest mixed Ga-P dimers on top of the Ga-terminated substrate as ground-state geometry for the cation-rich phase of GaP(001)(2×4). Our results indicate the formation of P dimers at the surface for the more anion-rich phase of GaP(001)(2×4). [S0163-1829(99)02828-3]

I. INTRODUCTION

Much progress has been made in recent years in understanding the microscopic structure of the growth planes of III-V compound semiconductors (for a recent review see, e.g., Ref. 1). This does not hold, however, for GaP. The experimental studies carried out so far arrive at different and partially contradicting conclusions about the symmetry and structure of the GaP(001) surface. In most publications, it has been suggested that ion bombardment and annealing of GaP(001) results in a $(4\times2)/c(8\times2)$ reconstructed, Ga-rich surface,[2–7] in analogy to the corresponding Ga-rich GaAs(001) surface structure.[8] A $(4\times2)/c(8\times2)$ reconstruction was also reported for Ga-rich GaP(001) prepared by decapping of P- and As-protective layers.[9] In that experiment, however, a residual As contamination was present on the surface. In gas source molecular-beam epitaxy (MBE) experiments[10] it was found that (2×4) and (4×2) reconstruction patterns correspond to P- and Ga-stabilized surfaces. In Ref. 4, on the other hand, clear differences between the scanning tunneling microscopy (STM) images recorded on sputtered/annealed GaP(001) surfaces and the corresponding data for GaAs(001)$(4\times2)/c(8\times2)$ surfaces[11] are reported. In a more recent publication by the same group,[12] examining the atomic structure by ion scattering, the symmetry was corrected to a (2×4). (2×4) reconstructions under Ga as well as under P supply were also observed in MBE experiments of Ref. 13. Additionally, the authors found an intermediate (4×4) reconstruction during layer growth and suggested the formation of Ga droplets on a (2×4) reconstructed surface for high amounts of Ga supply. In a recent atomic layer MBE work,[14] (2×2)- and (2×4)-reconstructions were observed by reflection high-energy electron diffraction for P- and Ga-rich surfaces, respectively.

Apart from the ambiguous findings for the symmetry of the stable GaP(001) surface, a wide variety of geometrical models were discussed for its surface structure: in analogy to GaAs(001), $\beta(4\times2)$, and $\beta2(4\times2)$ structures were suggested based on electron spectroscopy[9] and STM (Ref. 3) experiments, respectively. Basically the same structure, but with a much larger dimer separation, was put forward in Ref. 5. On base of time-of-flight scattering and recoiling spectroscopy a (2×4) Ga-trimer structure[6] was proposed, in analogy to according previous work on InP(001).[15] On the basis of ion scattering experiments a Ga double-layer structure[12] and, finally, in a very recent STM study a Ga single-dimer structure was suggested.[16]

Besides the puzzling experimental results there exists, to our knowledge, only one theoretical study[17] so far, based on a semiempirical method. In that work, several (2×4) dimer geometries are suggested. The energetic comparison, however, is complicated, since only desorption energies are given.

While the atomic surface structure of GaP(001) is still controversial, recent studies of In-rich InP(001) surfaces are available:[15,18–21] Experiments and calculations reveal that the microscopic structure of the cation-rich InP(001) surface differs from the well-investigated GaAs(001) surface[8,22,23] due to the large size difference between cations and anions. The size ratio between the covalent radii of cations and anions is

about 1.36 for InP compared to 1.19 for GaP and 1.05 for GaAs.[24] Based on the simple concept of covalent radii, GaP(001) surface structures can therefore be expected also to deviate from the ones observed for GaAs.

In the present paper, clean, reconstructed GaP(001) surfaces are characterized in ultra high vacuum (UHV) by low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and reflectance anisotropy spectroscopy (RAS). A variety of plausible structural models for (2×4) and (4×2) reconstructed surfaces are probed by *ab initio* total-energy calculations. For the energetically favored structures we compute the RAS spectra. The comparison of the experimental data with the calculated surface-phase diagram and optical spectra indicates the existence of at least two distinct (2×4) reconstructions.

II. EXPERIMENTAL

A. Surface preparation

The GaP(001) surfaces were prepared by thermal desorption of a protective arsenic/phosphorus double layer (cap) under UHV conditions. For this purpose homoepitaxial GaP epilayers were grown by metal organic vapor phase epitaxy (MOVPE) on highly *n*-doped GaP(001) substrates and capped *in situ* utilizing the photodecomposition of phosphine and arsine by an eximer laser source.[20,25] The thermal desorption of the protective arsenic/phosphorus layer was performed in UHV (base pressure $\leqslant 10^{-10}$ hPa) by annealing to 690 K using an indirect resistive heating. Surface stoichiometry was modified by successive annealing steps up to 1000 K (the sample was kept at constant final temperature for five minutes in each annealing step). For comparison, surfaces were also prepared by sputtering and annealing, following the same experimental conditions as reported in literature[2–7] (400-eV Ar^+ ions, annealing temperature 725 K). The GaP(001) surfaces were cooled down to room temperature and investigated by LEED, RAS, and AES.

B. Results

The decapped GaP(001) surfaces (after annealing to 690 K) show a $(2\times1)/(2\times2)$-like LEED pattern [see Fig. 1(a)], with clear (2×1)-spots plus additional weak streaks in the [110] half-order position. Corresponding diffraction patterns under P-rich conditions are also observed on InP(001) surfaces[26,27] which, according to a recent STM study,[26] are terminated by P-surface dimers arranged in different local structures. Annealing to 785 K leads to a (2×4) LEED pattern. Due to not fully resolved fractional order spots in the [110] direction, the LEED pattern of this surface does not allow us to distinguish clearly between a (2×4) and a $(2\times4)/c(2\times8)$ reconstruction [Fig. 1(b)]. Upon further annealing up to 1000 K the quality of the LEED pattern is improved. The former streaks develop into sharp spots indicating a pure (2×4) reconstruction [Fig. 1(c)]. Upon annealing to still higher temperatures the symmetry remains unchanged until the surface deteriorates by forming Ga droplets, as indicated by a metallic component in the Ga $3d$ core-level photoemission line (not shown here). The P/Ga ratio determined by AES at the (2×4) reconstructed surface for low-annealing temperatures (only slightly above 785 K) is very close to the one found on the stoichiometric balanced (110) cleavage surface of GaP. Upon annealing to higher temperatures (1000 K) the ratio changes successively by a factor of approximately two towards a Ga-rich surface, suggesting the existence of distinct (2×4)-reconstructions, being more P-rich at lower and more Ga-rich at higher annealing temperatures.

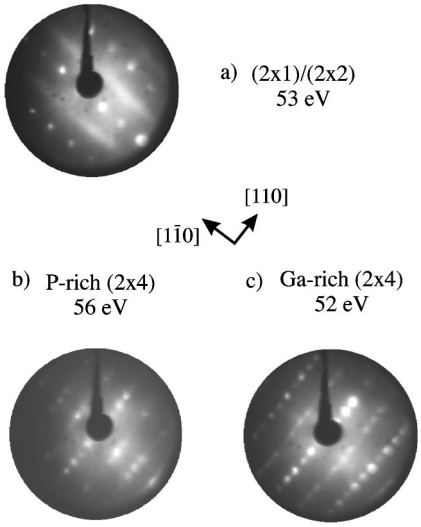

FIG. 1. LEED patterns recorded from GaP(001): (a) $(2\times1)/(2\times2)$-like taken at an electron energy of 53 eV, (b) P-rich (2×4) (electron energy 56 eV) and (c) Ga-rich (2×4) (electron energy 52 eV).

Real parts of different RAS spectra recorded from GaP(001) surfaces are shown in Fig. 2(a). For the sake of comparison, RAS spectra of the $(2\times1)/(2\times2)$-like and (2×4) InP(001) and the $\beta2(2\times4)$ GaAs(001) are shown in Fig. 2(b). Three different spectral line shapes are reproducibly observed on GaP(001), correlated with the surface preparation: characteristic spectra belonging to the $(2\times1)/(2\times2)$-like structure, the P-rich (2×4) structure at lower annealing temperature and the Ga-rich (2×4) structure at higher annealing temperature. The P-rich GaP(001) (2×4) surface (middle curve) shows a spectrum, which is qualitatively similar to the one observed for the As-dimer terminated $\beta2(2\times4)$ GaAs(001) surface.[28,29] It is characterized by pronounced maxima at 3.5 and 4.8 eV, close to the E_1 and E_0' gap energies of GaP (3.69 and 4.77 eV, respectively[30]) and a weak maximum between the gaps, at 4 eV. After annealing to higher temperatures the spectrum changes into a line shape similar to the one observed for the mixed In-P dimer terminated InP(001)(2×4) surface.[31–34] New features in this spectrum are a strong minimum at 2.4 eV and a maximum at 3.2 eV, significantly below the E_1 gap of GaP. The maxima around 4 eV and at 4.8 eV found on the P-rich (2×4) surface are still present.

A (2×4) LEED pattern is also observed from (001) surfaces prepared by sputtering and annealing. The P/Ga AES ratio on this surface is close to the one found at intermediate annealing temperatures (875 K) on the decapped surfaces. The RAS spectrum, however, corresponds to that of the Ga-rich structure of the decapped GaP(001) surfaces.

Summarizing the RAS results, there are clear similarities between GaP(001) and InP(001) for the very anion-rich

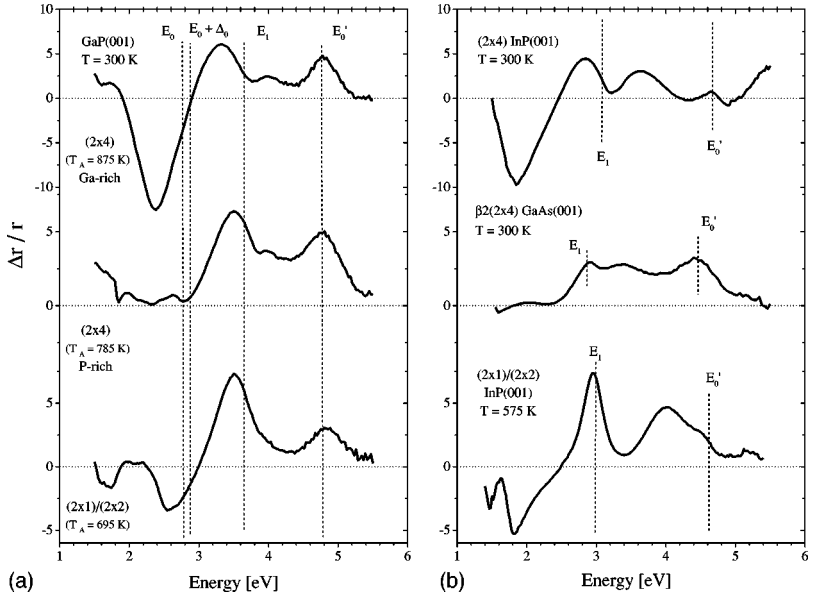

FIG. 2. Real parts of $[(r_{[1-10]}-r_{[110]})/\langle r\rangle]*10^3$ for: (a) GaP(001) for different annealing temperatures (LEED patterns and annealing temperatures are indicated in the plot) and (b) (2×4)InP(001) (upper curve), $\beta2(2\times4)$GaAs(001) (middle curve), and $(2\times1)/(2\times2)$-like InP(001) (lower curve).

$(2\times1)/(2\times2)$-like and the very cation-rich (2×4) reconstructed surfaces, in particular if one accounts for the different bulk critical-point energies of the two materials. The spectrum of the P-rich (2×4) reconstructed GaP(001) surface, however, resembles the one of GaAs(001)$\beta2(2\times4)$. The evolution of the RAS spectra with increasing Ga surface coverage implies that at least two distinct (2×4) structures with different stoichiometry exist on GaP(001). To address this question, we have performed *ab initio* calculations of the energetics and surface optical properties, which are presented below.

III. THEORY AND DISCUSSION

A. Computational

The calculations were based on density-functional theory in local-density approximation (DFT-LDA). The electron-ion interaction was described by nonlocal norm-conserving pseudopotentials.[35] The Ga $3d$ electrons are partially taken into account by means of a nonlocal core correction to the exchange and correlation energy. The electronic degrees of freedom were relaxed using a recently developed real-space multigrid technique.[36,37] This approach provides for effective convergence acceleration and preconditioning on all length scales. Furthermore, it allows for an efficient parallelization and is thus particularly suitable for large surface reconstructions as studied here. The spacing of the finest grid used to represent the electronic wave functions and charge density was determined through a series of GaP bulk calculations. We find structural and electronic properties to be converged for a spacing of 0.238 Å . This corresponds to an energy cutoff in plane-wave calculations of about 24 Ryd. Throughout the calculations we use the calculated equilibrium lattice constant of 5.39 Å , which is slightly smaller than the measured value [5.45 Å (Ref. 38)]. More severe is the underestimation of the electronic excitation energies due to the DFT-LDA band-gap problem. We determine the values of 1.46, 1.68, 2.09, and 3.97 eV for $E(X_{1c})$, $E(X_{3c})$, $E(\Gamma_{1c})$, and $E(\Gamma_{15c})$. These energies are about 0.7 – 0.9 eV smaller than measured. The same almost constant shift is observed for the E_0, E_1, and E_0' critical points of the bulk electronic structure, for which we calculate values of 2.1, 2.9, and 4.0 eV. To model the GaP(001) surface we consider a periodic super cell along the surface normal. It contains 8/12 atomic (001) layers and a vacuum region equivalent in thickness to 8 atomic layers for calculations of the energetic/optical properties. The dangling bonds at the bottom layer of the slab are saturated with pseudohydrogens. The geometries of the investigated models were relaxed until all calculated forces were below 25 meV/Å . Integrations in the surface Brillouin zone (SBZ) for calculating the atomic and electronic ground state of the surface were performed using four special **k** points in the irreducible part. For the calculation of the dielectric function we included all conduction bands within 8 eV of the top of the valence bands, using 16 uniformly distributed **k** points in the irreducible part of the SBZ. This corresponds to 256 **k** points in the full (1×1) SBZ.

B. Surface phase diagram

One essential ingredient for calculations of surface ground-state structures is the choice of appropriate starting geometries for optimization. This holds in particular for large surface reconstructions as studied here. Figure 3 gives a top view of the relaxed geometries of all structures considered in this work.

(001) surfaces of III-V compounds are usually explained in terms of the surface structures known from GaAs.[39] Therefore, the β, $\beta2$, α and anion-dimer models [Figs. 3(a), 3(b), 3(c), 3(j), 3(l), and 3(m)] suggested for GaAs (Refs. 1,8,22,23, and 40) were considered. On the other hand, as outlined in the introduction, the size difference between cations and anions may lead to GaP surface structures different from GaAs. In case of InP it was noted that the formation of

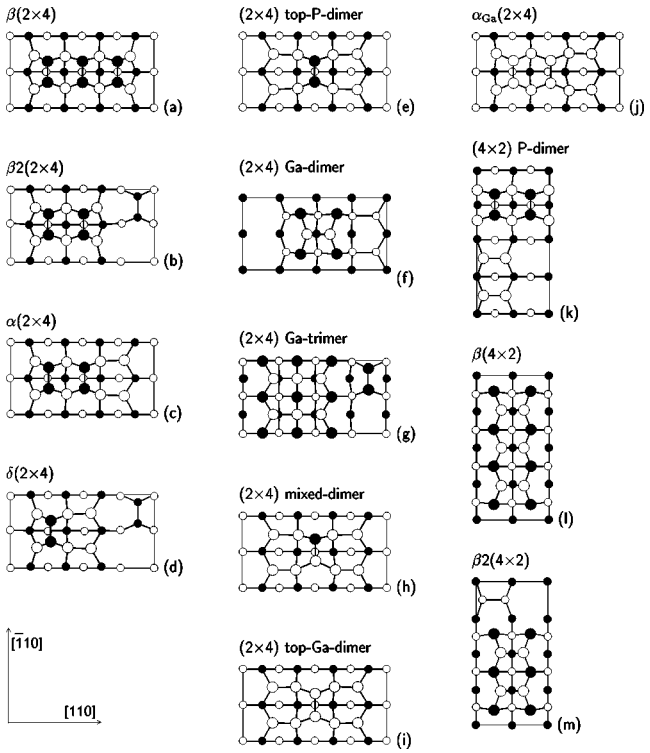

FIG. 3. Top view of relaxed GaP(001)(2×4) and (4×2) surface reconstruction models. Empty (filled) circles represent Ga (P) atoms. Large (small) symbols indicate positions in the first and second (third and fourth) atomic layers. (2×4) and (4×2) reconstructions are ordered by increasing Ga coverage.

sp^2-hybridized cation dimers at the surface causes appreciable stress in the subsurface layers due to the large size difference between the substrate constituents.[23] At this point, we want to emphasise further similarities between GaP and InP(001) surfaces: (i) The reconstructions evolve similarly from a (2×1)/(2×2)-like phase for anion-rich to (2×4) for more cation-rich surfaces, (ii) as discussed above, GaP and InP show similar features in their anisotropic optical response, and (iii) the surface core-level shifts measured for cation-rich InP and GaP surfaces are qualitatively very similar.[16,19] Thus, it appears plausible to include in our study also the single-dimer structures shown in Figs. 3(e), 3(h), and 3(i), which were assumed to exist on InP(001)[19]. These cation-rich structures allow to saturate all surface bonds and avoid or at least reduce the stress caused by the formation of cation-cation dimers. For the same reason also the δ structure [Fig. 3(d)], which is believed to describe the Sb-induced GaAs(2×4) reconstruction,[41] may be a plausible candidate. Besides the models mentioned above we include in our calculations also the structures Figs. 3(f), 3(g), 3(j), 3(k), and 3(l) which have been suggested for GaP(001) based on previous experimental work[3,5,6,9,12] (see Introduction). We would like to note that the model Fig. 3(f) corresponds to the structure of lowest energy we derive from the class of structures proposed in a recent STM study.[16] In our previous work on InP(001) an according structure was already tested and found to be energetically unfavourable.[19]

The investigated models realize different Ga coverages: $\Theta=1/4$[$\beta(2\times4)$ and $\beta2(2\times4)$], $\Theta=1/2$(α and δ), $\Theta=3/4$ [top-P-dimer, Ga-trimer, (2×4) Ga dimer, $\beta(4\times2)$ and $\beta2(4\times2)$], $\Theta=1$ (mixed-dimer), $\Theta=5/4$ for (top-Ga dimer) and $\Theta=6/4$ [$\alpha_{Ga}(2\times4)$].[42] An energetic comparison of these structures can therefore only be made by taking into account the chemical potentials of the surface constituents.[23] In Fig. 4, we show the relative formation energies of the considered surface structures vs the Ga chemical potential. For Ga-rich surfaces mixed Ga-P dimers on top of an Ga-terminated surface [Fig. 3(h)] are favoured. For less Ga-rich conditions P-dimers in a $\beta2(2\times4)$ geometry [Fig. 3(b)], known from As-rich GaAs(001) surfaces,[22,43] are stable. For intermediate values of the Ga chemical potential the $\delta(2\times4)$ phase [Fig. 3(d)] may occur. In the extreme Ga-rich limit the top-Ga-dimer model [Fig. 3(i)] is stable. Before comparing the calculated phase diagram with the experiments, we want to underline that only (2×4) and (4×2) reconstructions are addressed here. Other surface symmetries, which may be favored for very P-rich conditions, were not considered. The phase diagram in Fig. 4 agrees well with our experimental findings: (i) The stable, Ga-rich GaP(001) surface reconstructs in (2×4) symmetry. Among the (4×2) reconstructions the energetically most favored one, the GaP(001)$\beta2(4\times2)$ structure, is about 0.1 eV per surface atom higher in energy than the (2×4) top-P-dimer model. Therefore, it is very unlikely to be an equilibrium structure. (ii) Different (2×4) surface phases occur depending on the actual value of the Ga chemical potential, i.e., the surface preparation conditions. (iii) The phase diagram is very similar to that of InP(001),[19] as suggested by the evolution of the optical spectra discussed above. The similarity between the surface phase diagrams of InP and GaP is likely to be caused by the same mechanism: The size difference between anions and cations which favors the formation of single-dimer structures for cation-rich surfaces over the accomodation of sp^2-hybridized cation dimers that are typical for GaAs(001) surfaces. The δ, mixed-dimer and top-Ga-dimer models are characterized by strong Ga-Ga bonds (bond lengths 2.47 – 2.62 Å) in the second atomic layer. The dimer lengths are 2.44 Å for the Ga-Ga dimer of the top-Ga-dimer model, 2.23–2.25 Å for the P-P dimers of the $\beta2$ and δ structure, and 2.36 Å for the Ga-P dimer for the mixed-dimer model.

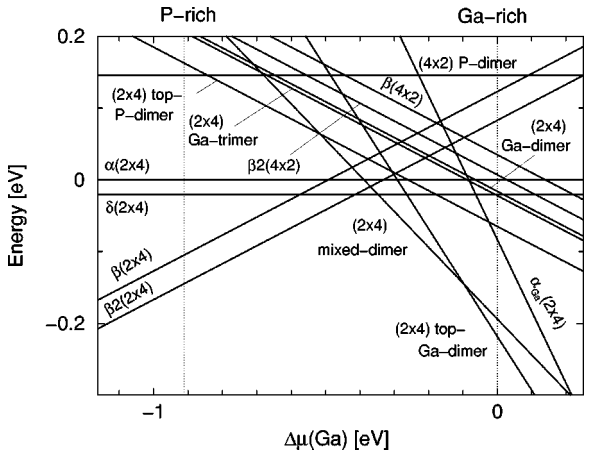

FIG. 4. Relative formation energy (with respect to the P-trimer structure) per (1×1) unit cell for GaP(001) surface reconstructions vs $\Delta\mu(\mathrm{Ga}):=\mu_{\mathrm{bulk}}(\mathrm{Ga})-\mu(\mathrm{Ga})$. The approximate thermodynamically allowed range: $-\Delta H_f(\mathrm{GaP})[=0.91$ eV (Ref. 51] $\leqslant\Delta\mu(\mathrm{Ga})\leqslant0$ is indicated by dashed lines.

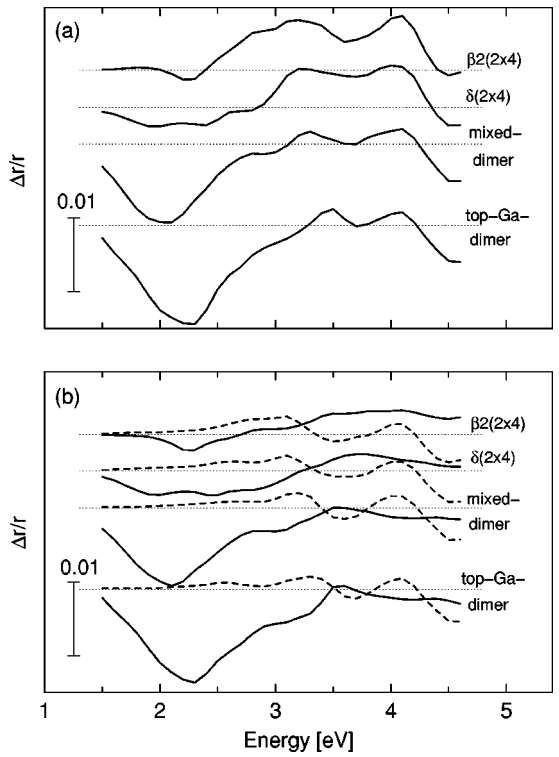

FIG. 5. (a): RAS spectra $\{\mathrm{Re}[(r_{[1-10]}-r_{[110]})/\langle r\rangle]\}$ calculated for the energetically favored structural models of the GaP(001)(2 $\times$4) surface. (b): Calculated RAS spectra considering only transitions within the uppermost four atomic layers (solid lines) and below the top four layers (dashed lines). The zero line in each spectrum is indicated by a horizontal dotted line.

These values are in good agreement with the sum of the respective covalent radii[24] and the corresponding bond lengths at GaAs(001) (Refs. 22,23, and 43) and InP(001) surfaces.[21] All equilibrium structures are in agreement with electron counting heuristics.[44]

C. Optical anisotropy

While the calculated phase diagram is in agreement with our experimental data, a more direct comparison between theory and measurement is desirable in order to identify specific surface structures. To this end we compute the reflectance anisotropy of the energetically favoured structures. The calculations are carried out in independent-particle approximation based on the electronic structure obtained within DFT-LDA. We follow the formalism developed by Del Sole[45] and Manghi *et al.*[46] Our calculations are on the same footing as a recent study of the optical properties of InP(001) surfaces,[34] where further details can be found.

The calculated spectra are shown in Fig. 5(a). The top-Ga-dimer, mixed-dimer, and δ structures show a pronounced negative anisotropy in the low-energy region, with minima between 2.0 and 2.3 eV. The strength of that anisotropy is directly correlated to the number of Ga-Ga bonds along the [110] direction. Its magnitude is highest for the top-Ga-dimer model with eight bonds, slightly reduced and shifted to lower energies for the mixed-dimer geometry with six cation-cation bonds and flattened for the δ structure with only two such bonds. The calculated spectra also show a strong dependence on structural details for higher energies. For the $\beta 2$ geometry with three P-P dimers oriented along $[1\bar{1}0]$ we find a relatively broad positive anisotropy between about 2.4 and 4.4 eV. Maxima of the anisotropy appear around 3.2 and 4.1 eV and a shoulder exists at 2.8 eV. The shape of that anisotropy is roughly preserved for the δ structure, which features one P-P dimer. The magnitude of the anisotropy, however, is somewhat reduced and the spectrum is shifted downwards. An even further reduction in positive anisotropy occurs for the mixed-dimer and top-Ga-dimer structures, featuring single Ga-P or Ga-Ga dimers, respectively, on top of a Ga-terminated substrate. The described evolution of the spectra in the high-energy region shows thus a correlation between the positive anisotropy and the formation of P-P dimers.

In order to better understand the origin of the surface anisotropy we performed further calculations. Figure 5(b) shows the calculated RAS for the four surface geometries taking into account only transitions within the uppermost four atomic layers. These are the layers where most of the surface related structural and electronic modifications occur. The calculated spectra are rather similar to those calculated for the complete slab. In particular, this holds for the negative anisotropy around 2 eV, which can therefore be attributed to near-surface transitions. A similar feature at InP(001) was explained by transitions between cation-cation bonding states and empty dangling bonds at threefold coordinated surface cations.[34] The anisotropies at higher energies are less well reproduced by near-surface transitions. We find a relatively broad positive anisotropy above 3.3 eV for the $\beta 2$ and δ structures, which is absent for mixed-dimer and top-Ga-dimer structure. In a recent study of InP(001) (Ref. 34) this anisotropy was traced back to transitions between occupied anion-dimer states and unoccupied surface resonances. Also shown in Fig. 5(b) are the contributions to the optical anisotropy due to transitions below the uppermost four layers (dashed lines). For all investigated structures these transitions between predominantly bulklike states give rise to features at the bulk critical points that depend only weakly on the surface structure and stoichiometry. In particular, all curves show minima around 3.6 eV and maxima at about 4.1 eV, close to the calculated E_0' gap. This reflects the general trend that surface transitions often dominate the low-energy part and bulklike transitions are more pronounced in the high-energy part of the RAS spectra.

The comparison with the experimental spectra is complicated by the DFT-LDA band-gap problem. As discussed above, a redshift of about 0.7 – 0.9 eV for the bulk-related features arises from the underestimation of the bulk excitation energies. This shift does not necessarily apply to the transitions between surface states. Quasiparticle calculations for semiconductor surfaces including many-body effects in GW approximation[47–49] have shown that bulk- and surface-state energies may experience different shifts with respect to the eigenvalues of the underlying DFT-LDA calculation. In particular, Hybertsen and Louie[47] point out that, depending on the orbital character of the specific states, the surface band gap may actually open much less than the bulk gap, when self-energy effects are included in the calculations. Electron-hole interaction effects[50] can also be expected to change the position and magnitude of anisotropy features. Unfortunately, both self-energy and electron-hole interaction

effects are beyond the scope of our work. If these limitations are borne in mind, however, a meaningful comparison between experimental and calculated spectra can still be made. The RAS spectrum measured for the (2×4) structure prepared at higher annealing temperature (Ga-rich phase) features a strong negative peak in the low-energy region. Given the energy position of this peak and its dependence on the preparation conditions, it is very likely that it is surface related and can be identified with the calculated negative anisotropy arising from Ga-Ga bonding related states described above. Both the top-Ga-dimer model and the mixed-dimer model thus appear plausible candidates to explain the Ga-rich surface phase. The measured spectrum for the Ga-rich phase shows further maxima between the energies of the E_0 and E_1 critical points and at the E_0' bulk peak. The latter maximum at the corresponding energy of about 4 eV is present in the calculated spectra of all considered structures. The first peak, which should be observed between 2.1 and 2.9 eV in the calculated spectrum, is completely absent in case of the top-Ga-dimer structure; it appears, however, as a weak shoulder for the mixed-dimer model. Therefore we identify the Ga-rich phase of the GaP(001)(2×4) surface tentatively with the mixed-dimer model. This assignment is corroborated by very recent surface core-level shift measurements on Ga-rich GaP(001)(2×4) surfaces,[16] where one P2p and two Ga3d surface components were found. The Ga-surface components were assigned to threefold coordinated Ga atoms and Ga-Ga bonds. These two components can be explained both by the top-Ga-dimer structure and the mixed-dimer model. Only the latter, however, provides an explanation for the finding of a surface P component, supposed to arise from threefold coordinated P atoms.

The measured spectrum for the (2×4) structure annealed at lower temperature (less Ga-rich phase) is dominated by a ''camelback'' overall spectrum shape with maxima between the energies of the E_0 and E_1 critical points and at the E_0' bulk peak. No negative anisotropy appears. The only computed spectrum with no (or very little) negative anisotropy belongs to the $\beta2(2\times4)$ structure. Maxima appear at 3.2 and 4.1 eV, close to the calculated energies of the E_1 and E_0' critical points. Our results thus indicate that the P-rich phase of the GaP(001)(2×4) surface corresponds to the $\beta2(2\times4)$ structure in analogy to As-rich GaAs(001) surfaces.

IV. CONCLUSIONS

In conclusion, we have presented a comprehensive study of the atomic structure of (2×4) reconstructed GaP(001) surfaces based on electron spectroscopy, the investigation of the optical anisotropy and the energetics of the surface. Both for a balanced surface stoichiometry and for Ga-rich conditions, we find (2×4) reconstructed surfaces that are stabilized by the formation of dimers. Experiment as well as theory suggest the existence of at least two different (2×4) surface phases, depending on the Ga content of the surface. Our results indicate that mixed Ga-P dimers on top of an Ga-terminated surface are the ground state of the Ga-rich phase, analogously to InP(001)(2×4). For the less Ga-rich surface phase we suggest the formation of P-P dimers in a $\beta2(2\times4)$ geometry, as observed for GaAs.

ACKNOWLEDGMENTS

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