P-rich GaP(001)(2×1)/(2×2) surface: A hydrogen-adsorbate structure determined from first-principles calculations

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We perform first-principles total-energy and electronic structure calculations in order to determine the atomic structure of the P-rich (2×1)/(2×2) reconstruction commonly observed for GaP(001) surfaces grown by gas-phase epitaxy. A monolayer of buckled phosphorus dimers stabilized by hydrogen adsorbed in an alternating sequence is found to be energetically stable and to be consistent with the experimental data.

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In the last few decades intensive research has focused on III-V(001) surface structures. A few simple principles explain most of the large variety of stoichiometry-dependent surface reconstructions.[1,2] (i) The exposed surface atoms dimerize, in order to reduce the number of unsaturated surface dangling bonds. (ii) The electron counting principle postulates uncharged and semiconducting surfaces, with empty cation dangling bonds and filled anion dangling bonds. This leads to vacant dimer sites, i.e., surface reconstructions due to missing dimers.[3] (iii) The spatial arrangement of dimers and missing dimers is largely determined by their electrostatic interaction.[2,4]

Some surface structures, however, remain unresolved, while others seemingly violate the empirical rules summarized above. This concerns in particular reconstructions which form under very cation-rich[5,6] or very anion-rich preparation conditions.[7] The GaP(001)(2×1)/(2×2) surface observed for specific anion-rich preparation conditions is one example of a hitherto unresolved III-V(001) surface structure. III-V(001) surface reconstructions smaller than (2×4) necessarily violate the electron counting principle.[3] The observation of a (2×1)/(2×2) reconstruction is thus not in accord with the empirically found principles governing the stability of III-V(001) surfaces. It has been tentatively attributed to surface termination by either P-P dimers[8–11] or mixed Ga-P dimers.[12] A large number of plausible (2×1) and (2×2) surface geometries were probed by first-principles calculations.[13,14] The energetically most favorable structures are the formation of one or two P-P dimers on top of a completely P-covered GaP(001)(2×2) surface. However, the $c(4\times4)$ reconstructed GaP surface is substantially lower in energy than the (2×2) surface (cf. Figs. 1 and 2 in Ref. 2). We are aware of only one experimental study reporting a (4×4) reconstructed GaP surface, though.[15] Interestingly, the authors of this study used solid-source molecular beam epitaxy (MBE) to prepare their sample. P-rich surfaces prepared using either chemical beam epitaxy (CBE) (Refs. 11,16) or metal organic vapor phase epitaxy (MOVPE) (Refs. 9,10,17,18) seem to show (2×1)/(2×2) rather than (4×4) translational symmetries. The observation of a (2×1)/(2×2) surface could therefore be an artifact of remaining adsorbates such as hydrogen related to the surface preparation procedures. While hydrogen is present in MOVPE and CBE, it is absent under MBE conditions.

Recently it could be shown that the supposedly clean InP(001)(2×1) surface is not at all a clean surface, but hydrogen induced.[19] Here we explore the possibility that similarly the (2×1)/(2×2) reconstructed GaP(001) surface is a hydrogen-adsorbate structure.

Our calculations are based on a massively parallel, real-space finite-difference implementation[20] of the density-functional theory in the local-density approximation (DFT-LDA). A multigrid technique is employed for convergence acceleration. The computational details are similar to those in Ref. 2. We investigate more than 40 plausible structures which differ with respect to their geometries and their stoichiometries. The energetically favored hydrogen-induced surface reconstructions are shown in Fig. 1. The notation of surface structures is such that a leading P indicates adsorption on top of a P-terminated substrate and a hyphen followed by P, D, or MD denotes adsorption of P atoms, P dimers, or mixed Ga-P dimers, respectively. The number of hydrogens per surface unit cell concludes the notation.

Due to the varying surface stoichiometry, the thermodynamic grandcanonical potential Ω in dependence upon the chemical potentials μ of the surface constituents needs to be calculated in order to determine the surface ground state. The Ga and P chemical potentials cannot vary independently, because the surface is in equlibrium with bulk GaP. Correspondingly, it holds $\mu(\mathrm{Ga})+\mu(\mathrm{P})=\mu(\mathrm{GaP})_{\mathrm{bulk}}$, and the surface phase diagram may be shown in dependence on only two variables, which we take to the the chemical potentials

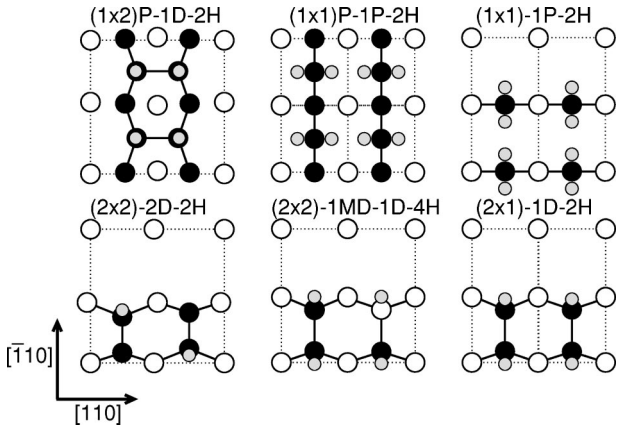

FIG. 1. Top view of relaxed GaP(001):H surface structures. Empty (filled, grey) circles represent Ga (P,H) atoms. The surface unit cells are indicated.

of Ga and H, see Fig. 2. Here $\Delta\mu(\mathrm{H})=0$ corresponds to the situation where the surface is exposed to molecular hydrogen at $T=0$. However, due to the need to overcome the dissociation barrier, the surface structures which are stable according to the calculated phase diagram will not necessarily form immediately. The surface phase diagram will change for higher temperatures, due to vibrational contributions to the energy and entropy of the surface structures, and due to the temperature and pressure dependence of the chemical potentials of the surface constituents. By far the largest change of the surface energetics is related to the hydrogen chemical potential. The temperature and pressure dependence of $\Delta\mu(\mathrm{H})$ can be approximated by that of a biatomic ideal gas.[21] A hydrogen chemical potential $\Delta\mu(\mathrm{H})$ of roughly -1 eV corresponds to typical MOVPE growth conditions. If no hydrogen is present, i.e., for $\Delta\mu(\mathrm{H})\ll 0$, GaP forms the surface reconstructions typical for the clean surface.[2] The structures stable for $\Delta\mu(\mathrm{H})>0$ may form if atomic hydrogen is available.

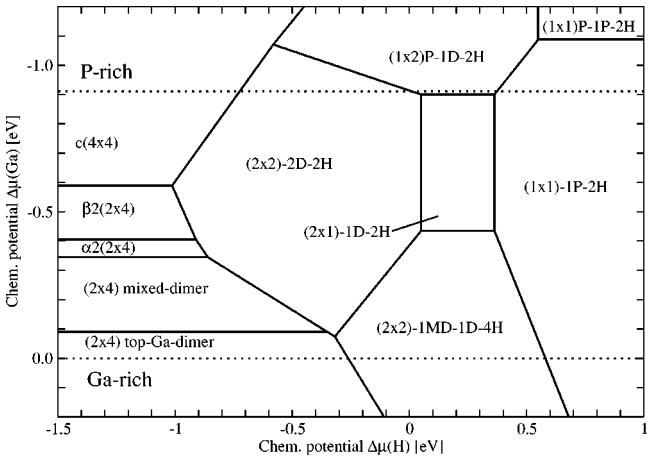

FIG. 2. Calculated phase diagram of the hydrogen exposed GaP(001) surface. Dotted lines indicate the approximate range of the thermodynamically allowed values of $\Delta\mu(\mathrm{Ga})$. The chemical potential of hydrogen $\Delta\mu(\mathrm{H})$ is given with respect to molecular hydrogen.

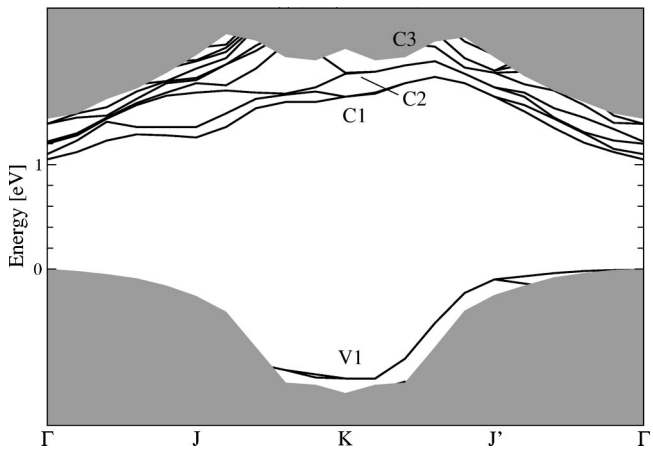

FIG. 3. Surface band structure for the (2×2)-2D-2H surface. Grey regions indicate the projected bulk band structure. ΓJ and $\Gamma J'$ lines are parallel to [$\bar{1}$10] and [110], respectively.

The phase diagram is rather similar to recent results for InP:H.[19] In particular the (2×2)-2D-2H surface, i.e., the periodic arrangement of oppositely buckled ($\Delta z=0.32$ Å) P dimers on top of a cation-terminated substrate, is energetically favored. One H atom is bonded to the ''down'' atom of the P dimer. This structure should form for P-rich to moderately Ga-rich preparation conditions, as long as molecular hydrogen (or atomic hydrogen at elevated temperatures) is available. It may thus be expected to describe the surface prepared by annealing GaP(001) samples grown in the presence of hydrogen, i.e., in gas-phase epitaxy.

While the 2D-2H structure seems to represent the surface ground state for annealed gas-phase epitaxy grown GaP(001) surfaces, energetical arguments alone are only one indication that this structure corresponds to the surface observed experimentally. Its formation may be kinetically hindered. In order to clarify whether the 2D-2H structure indeed corresponds to the experimental observations, we investigate its spectroscopic signatures.

The model obeys the electron counting rule. Its surface bands calculated along the high-symmetry lines of the (2×2) surface Brillouin zone are shown in Fig. 3. The surface band gap calculated in DFT-LDA is slightly larger than one eV. Based on the calculated surface electronic structure we simulate scanning tunneling microscopy (STM) images for bias voltages of ±3.5 V according to the Tersoff-Hamann approach.[22] The filled state image, shown in Fig. 4(a) shows excellent agreement with the STM image of the P-terminated surface measured at sample bias -3.35 V (cf. Fig. 1 in Ref. 18). In both the measured and simulated STM images zig-zag chains running along the [110] direction are observed. The bright spots forming the zig-zag pattern are due mainly to the electron lone pair at the ''up'' atom of the P dimer. This state, $V1$ in Fig. 3, forms the uppermost occupied surface band. The energetically well separated hydrogen-phosphorus bond at the ''down'' atom explains why only one P atom is seen in the STM experiment. Zig-zag chains are also predicted for empty-state images [cf. Fig. 4(b)].

Reflectance anisotropy spectroscopy (RAS) is particularly suitable for surface structure exploration during epitaxial

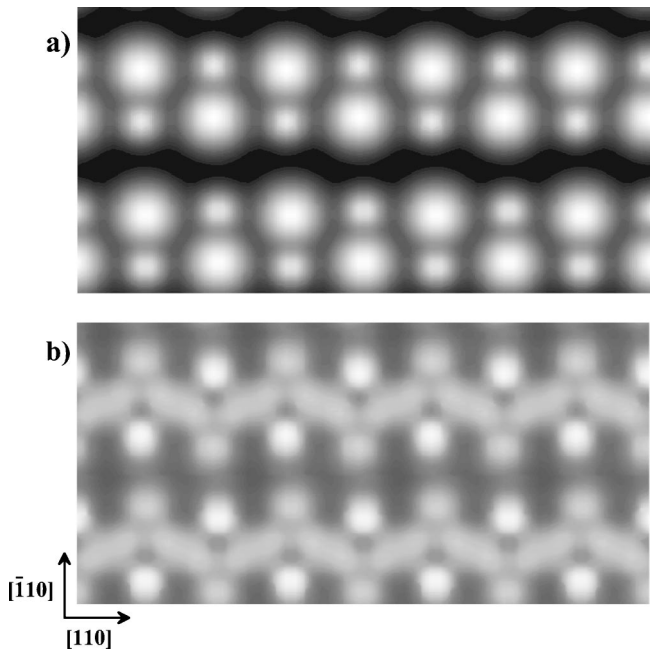

FIG. 4. Calculated STM image of the P monolayer-terminated GaP(001) surface, consisting of oppositely buckled dimers, with hydrogen attached to the ''down'' atom. (a) Filled states image; (b) empty states image. An area corresponding to 15.4×30.8 Å^2 is shown.

growth. In contrast to most other surface analysis techniques, it may also be used in gas-phase epitaxy conditions. The measured RAS spectrum of the $(2\times1)/(2\times2)$ ordered GaP(001) surface features a characteristic minimum/maximum structure with peak positions at 2.3–2.6 and 3.4–3.7 eV, respectively.[10,11,18,23] Measured RAS data from Refs. 10,11,18 are shown in Fig. 5. It is obvious that there is some scatter in the data. On one hand, this is related to temperature

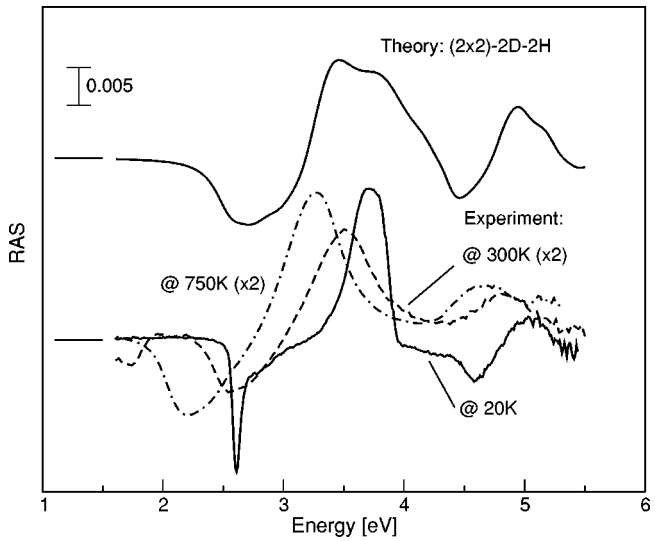

FIG. 5. RAS spectra $[\mathrm{Re}\{(r_{[1\bar{1}0]}-r_{[110]})/\langle r\rangle\}]$ for P-terminated GaP(001)$(2\times1)/(2\times2)$ surfaces measured at 20 K (Ref. 18), 300 K (Ref. 10), and 750 K (Ref. 11) are compared with the spectrum calculated for the 2D-2H structure of GaP(001).

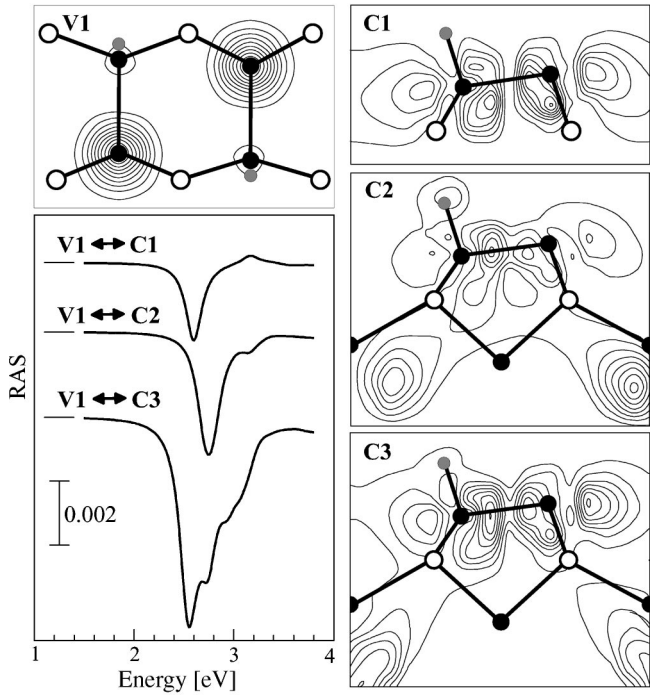

FIG. 6. Calculated RAS due to transitions between specific surface states as indicated. The orbital character of the corresponding states at the K point of the surface Brillouin zone is shown ($V1$: top view, $C1-C3$: side views). The notation corresponds to Fig. 3.

effects, which lead to a peak broadening and a redshift. In addition different preparation conditions may be responsible. The data of Ref. 10 were obtained from surfaces prepared by thermal desorption of a protective As/P double layer from MOVPE-grown GaP(001). The spectrum from Ref. 11 was recorded directly in the CBE system. In the same work Zorn *et al.* present a spectrum taken in MOVPE, which has nearly the same line shape. Töben *et al.*[18] combined low-temperature RAS with low-energy electron diffraction (LEED) and STM to characterize their MOVPE-grown sample. Therefore the RAS spectrum measured at 20 K can be unambigously attributed to GaP(001)$(2\times1)/(2\times2)$ surfaces showing zig-zag chains running along the [110] direction.

Figure 5 also contains the RAS spectrum calculated according to the scheme devised in Refs. 24–26 for the 2D-2H model. In the calculations we approximate self-energy effects by using a rigid shift of 0.8 eV, which is the value we obtain for the GW corrections in GaP bulk.[27,28] The calculated peak positions should be compared to the low-temperature experiment. We used an energy broadening of 0.15 eV in order to account for the finite number of **k** points [a set equivalent to 1024 points in the full (1×1) surface Brillouin zone was used]. This does not allow for the accurate reproduction of the sharp low-temperature features. Excitonic and local-field effects in the optical spectra[29,30] as well as the influence of surface defects are neglected in the calculations. Bearing all these restrictions in mind, the RAS spectrum calculated for the 2D-2H model reproduces the experiments very well. The 2D-2H structure favored from total-energy calculation thus explains the experimental find-

ings available for the $(2\times1)/(2\times2)$ ordered GaP(001) surface.

While the optical anisotropy features above the E_0 critical point energy of GaP are relatively weakly affected by the surface geometry and stoichiometry, the RAS minimum at around 2.3–2.6 eV can be considered a fingerprint for the P-rich $(2\times1)/(2\times2)$ reconstructed surface.[10,11] In order to better understand the origin of this feature, we calculate the optical anisotropy due to transitions between pairs of surface states. We find that some of these transitions give rise to strong anisotropy features, as shown in Fig. 6. There we plot the RAS due to transitions between the uppermost occupied surface state $V1$ and the lowest conduction states, $C1-C3$. It is obvious that in particular the transitions between the electron lone pair at the ''up'' atom of the P dimer into the surface resonant state $C3$ are responsible for sizable contributions to the low-energy fingerprint of the P-rich GaP $(2\times1)/(2\times2)$ surface.

In conclusion, based on total-energy calculations as well as simulated STM images and RAS spectra we suggest that the well-ordered P-rich GaP(001)$(2\times1)/(2\times2)$ surface reported in many gas-phase epitaxy studies does not correspond to the clean surface, but is formed by surface termination with half a monolayer of hydrogen. All previously reported experimental findings for this surface can be explained on the basis of the GaP(001):H structure derived here. The 2D-2H model complies with the electron counting rule. Its characteristic low-energy feature in the surface optical anisotropy is related mainly to transitions between surface P lone pairs of electrons and empty surface resonances.

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