Clarification of the GaP(001)(2×4) Ga-rich reconstruction by scanning tunneling microscopy and *ab initio* theory

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We infer the structure of the GaP(001)(2×4) surface from a study of scanning tunneling microscopy (STM) images obtained under UHV conditions on metal-organic vapor phase epitaxy grown samples. STM images are compared with results of first-principles calculations for models energetically most favorable under Ga-rich growth conditions. The comparison shows that the GaP(001)(2×4) surface unit cell consists of a mixed Ga-P dimer on top of a complete gallium layer, hence ruling out the Ga-Ga dimer model.

Because of their favorable properties for optoelectronics, the phosphorus-based zinc-blende III-V semiconductors InP, GaP, and InGaP have become technologically more important during the last decade. Despite this importance, little is known about their surfaces and surface structures, particularly their polar (001) faces, in contrast to the group-III arsenides, typified by GaAs(001). The surface reconstructions of the latter have been considered to provide a general model representing the other III-V compound semiconductors, too. Up to now most studies involving the surface structures of the phosphides have been performed on InP(001). It has been demonstrated that the most In-rich surface reconstruction shows a (2×4) translational symmetry and can be explained by the so called mixed dimer model.[1] Within this model a mixed In-P dimer oriented along the $[\bar{1}10]$ direction is on top of a complete In layer. This surface reconstruction, in contrast, is not found on GaAs(001), where the most Ga-rich reconstruction is a (4×2) one.

For GaP(001) a variety of translational symmetries has been observed experimentally by electron diffraction methods such as low-energy electron diffraction (LEED) or reflection high-energy electron diffraction.[2–7] Additionally, other surface sensitive techniques have been applied to study these surfaces, including scanning tunneling microscopy (STM),[6] ion scattering spectroscopy,[4,5] and reflectance anisotropy spectroscopy (RAS).[7,8] It has been suggested that ion bombardment and annealing (IBA) of GaP(001) results in a Ga-rich (4×2) reconstruction by analogy with the Ga-rich GaAs(001) surface.[2,4] However, more recently this Ga-rich stable structure prepared by IBA was identified to be of a (2×4) symmetry.[5–7] Surfaces prepared using either solid-source molecular beam epitaxy,[3] chemical beam epitaxy, or by thermal desorption of a protective arsenic/phosphorus double layer[7,8] also indicated a (2×4) translational symmetry. In the last case the GaP epilayers were grown by means of metal-organic vapor phase epitaxy (MOVPE). Thus it can be concluded that the most stable Ga-rich surface reconstruction of GaP(001) is a (2×4) one, similar to InP(001).[1] Apart from the translational symmetry of the stable Ga-rich GaP(001) surfaces, the actual atomic structure is an open question. Various geometrical models have been discussed.[7] All these structures are based on Ga-Ga, P-P, or Ga-P dimers.

Total energy calculations show that under Ga-rich conditions only those (2×4) reconstructions are stable that consist of either Ga-P (mixed dimer) or Ga-Ga (top Ga dimer) dimers on top of a complete Ga layer[7] (see Fig. 3 below). The comparison of calculated and measured RAS spectra[7–9] favors the mixed-dimer structure for the (2×4) reconstruction, but cannot result in a final conclusion. In this paper a comparison of measured and calculated STM images is utilized to clarify the structure of the Ga-rich GaP(001)(2×4) surface.

In the following, the experimental STM results are discussed first, followed in the second section by *ab initio* calculation of STM images for the two possible (2×4) atomic surface structures. GaP layers were grown by MOVPE with phosphine (PH_3) and trimethylindium (TMIn) as precursors at a temperature of 650 °C on S-doped ($n = 5\times10^{18}\,\mathrm{cm}^{-3}$)

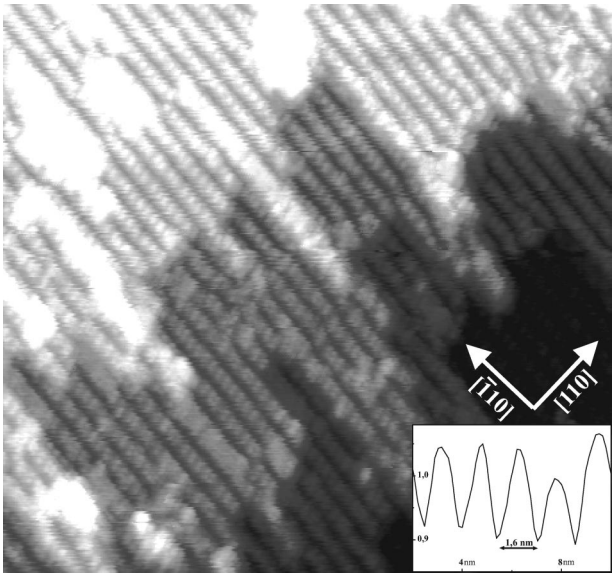

FIG. 1. Filled state STM image obtained after annealing the GaP(001) sample at 450 °C. The scan area is 420×440 Å, sample bias −3.5 V. The bright rows extending along the $[\bar{1}10]$ direction are separated by 15.6 Å, corresponding to a fourfold surface lattice constant. The inset shows a line scan along one of the rows, in the [110] direction.

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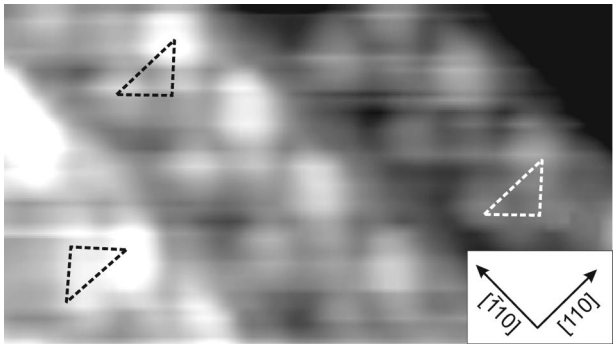

FIG. 2. High-resolution filled state STM image, scan area 44.5×27.5 Å, sample bias −3.5 V. The triangularlike structures in the bright rows, indicated by dashed lines, are clearly resolved.

epiready GaP(001) substrates. Since the MOVPE apparatus is not connected to an UHV analysis vessel, the samples were capped by an amorphous As/P double layer directly after growth in order to protect them before transport through air. Under ultrahigh vacuum conditions the amorphous protection layer was thermally desorbed at 400 °C and the sample with the surface exposed was annealed at 450 °C for approximately 10 min. The evolution of the (2×4) surface reconstruction was monitored by RAS. All experiments were performed at a base pressure of about 2×10^{-10} mbar. STM images were taken in constant current mode with an Omicron STM1. The bias values refer to the sample voltage with respect to the STM tip.

The RAS spectrum, taken after annealing, was in good agreement with RAS spectra for the (2×4) reconstruction obtained under growth conditions.[10] The LEED pattern showed a clear (2×4) periodicity. The $\frac{1}{4}$ order spots are intense and are accompanied by $\frac{1}{2}$ order streaking in the [110] direction.

In Fig. 1 a large scale STM image of the surface after annealing is shown. The image was taken at a sample bias of −3.5 V, allowing filled states to contribute. A rowlike structure in the $[\bar{1}10]$ direction is clearly observed. The rows are separated by 15.6 Å, corresponding to a fourfold surface lattice constant as can be seen from the line scan perpendicular to the rows (see inset of Fig. 1). The surface appears atomically flat within the range of the STM image containing a few monatomic terraces. In Fig. 2 a filled state STM image with atomic resolution at the same bias is shown. An additional triangularlike structure along the rows is well resolved within this image. The single triangles are separated by 8.1 Å, corresponding to a twofold lattice constant, and consist of a center structure (''head'') and two side structures (''ears''). The ''ears'' are separated by approximately 5.7 Å. This structure is quite similar to the one observed for the InP(001)(2×4) reconstruction[1,11] which was explained by the mixed-dimer model.[12,13]

In order to interpret the STM images on GaP(001), *ab initio* calculations of the electron density were performed. The electron wave functions were calculated using density functional theory (DFT) within the local density approximation (LDA).[14] The electron-electron interaction was described using the Perdew-Zunger extrapolation. The electron-ion interaction was treated by using norm-conserving, fully separable pseudopotentials.[15,16] Because of the shallow Ga 3*d* electrons, nonlinear core corrections were included. The single-particle wave functions were expanded into plane waves. They were restricted by a kinetic energy cutoff of 18 Ry. A Car-Parrinello-like method was used to minimize the total energy with respect to the ionic and electronic degrees of freedom.[16] The theoretical lattice constant obtained for the GaP bulk is 5.42 Å, which shows good agreement with the experimental one of 5.45 Å.

The GaP(100)(2×4) surfaces were simulated using repeated slabs of eight atomic layers, plus four layers of vacuum. One side of the slab was saturated with pseudohydrogen.[17] The two energetically most favorable (2×4) struc-

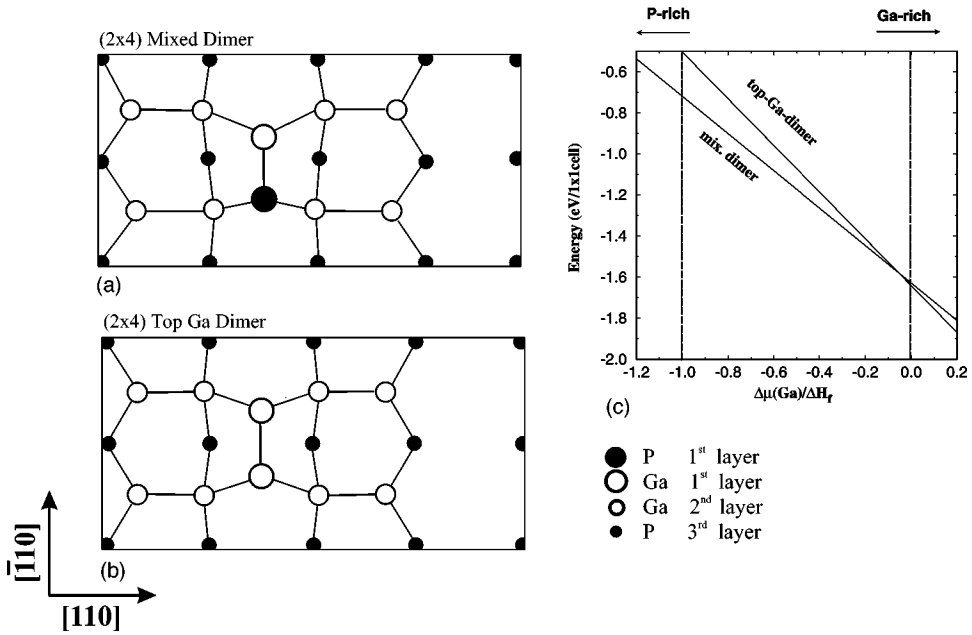

FIG. 3. Top view of the two surface geometries for the Ga-rich GaP(001)(2×4) surface: (a) mixed dimer; (b) top Ga dimer. (c) Surface energy for both structures versus the Ga chemical potential. The energy zero is taken at the ideal P-terminated structure.

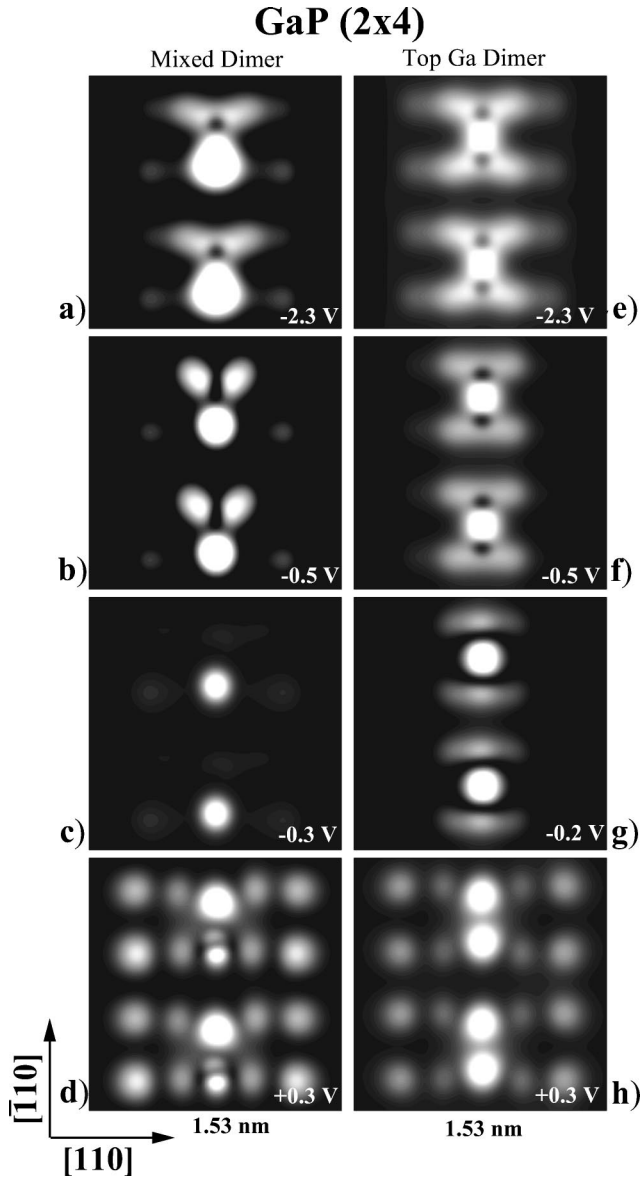

FIG. 4. Calculated STM images for the mixed-dimer and top-Ga-dimer geometries at different energies, with respect to the valence band maximum for negative voltages and with respect to the conduction band minimum for positive voltages.

tures appearing in the phase diagram [Fig. 3(c)] for very high Ga-rich growth conditions were considered: the (2×4) mixed dimer and the (2×4) top Ga dimer. The (2×4) mixed dimer [Fig. 3(a)] consists of a Ga-P dimer on top of a complete Ga layer. The (2×4) top-Ga-dimer structure, instead, is formed by a complete monolayer of Ga with an additional gallium dimer on top [Fig. 3(b)]. For extreme Ga-rich growth conditions the top-Ga-dimer structure is predicted to be more stable than the mixed-dimer one [see Fig. 3(c)].

The optimization of the structures was performed by relaxing the atoms until the interatomic forces became less than 0.025 eV/Å. Four special **k** points in the irreducible part of the Brillouin zone were used. The resulting structural parameters for the GaP(001)(2×4) surfaces are in good agreement with already published ones.[7,9] In the case of the GaP(100)(2×4) top Ga dimer, the Ga-Ga dimer bond

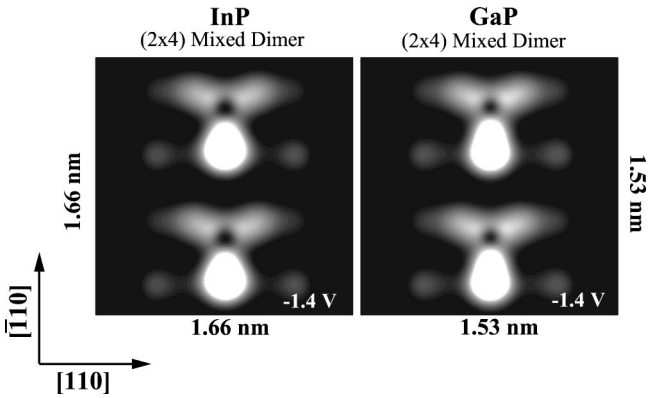

FIG. 5. Filled state STM images calculated for InP(001) and GaP(001) in the mixed-dimer reconstruction.

length is 2.47 Å, slightly smaller than the sum of the covalent radii (2.52 Å). The Ga-P dimer of the (2×4) mixed-dimer structure, with a bond length of 2.36 Å, displays a buckling with an angle of 9.51° (i.e., the P atom is 0.39 Å above the Ga atom).

Once DFT-LDA electron wave functions for the reconstructed surface were calculated, it was possible to simulate STM images using the Tersoff-Hamann approach.[18] In this approach, which resembles ordinary first order perturbation theory in the limit of low temperature and an arbitrarily localized tip, the tunneling current is proportional to the local electron density of states integrated over the energy bands that fulfill the selection rules of a tunneling process. In order to take into account the extent of a real tip, the local electron density of states was integrated in space between 1 and 3 Å above the surface. Depending on the number of energy bands that are summed, STM images corresponding to different voltages (applied to the sample with respect to the tip) can be simulated. In the case of filled states the sum was made from the valence band maximum (VBM) to a chosen energy in the valence bands. To make an alignment with respect to the voltage used in the experiment, the theoretical voltage can be obtained by adding to the energy used in the integration the energy difference between the experimental Fermi level and the VBM (about 1.2 eV).

In Fig. 4 the simulated STM images of both the mixed-dimer and the top-Ga-dimer reconstructions on GaP(100) are shown. For the occupied states we have selected energy intervals of 0.3 (0.2 eV for the top Ga dimer), 0.5 and 2.3 eV below the VBM, whereas for the unoccupied states an energy of 0.3 eV above the conduction band minimum was chosen. The simulated filled state STM images of the mixed dimer (2×4) GaP surface at higher voltages [Fig. 4(a) and 4(b)] show rows in the [$\bar{1}$10] direction containing a triangular structure that repeats every two surface lattice constants. This triangular structure shows only a weak dependence upon the voltage used. This is caused by the fact that for these voltages the most contributing surface states are always within the integration range. The more intensive circlelike spot (''head'') of this structure is formed by the dangling bonds at the P atom of the mixed dimers. This dangling bond is filled with two electrons and represents the highest occupied band. Thus at very small negative voltages [Fig. 4(c)] only the ''head'' can be seen. The ''ears'' of the structure originate from the filled backbonds between the Ga atom in

the mixed dimer and neighboring Ga atoms in the atomic layer beneath. With increasing voltages the shape of the ''ears'' changes gradually from the intense diagonal oval spots at -0.5 eV into features nearly perpendicular to the rows at -2.3 eV below the VBM.

In contrast, the simulated filled state STM images of the top-Ga-dimer reconstruction [Figs. 4(e) and 4(f)] contain a symmetric X pattern that is visible within the rows. Also, this pattern shows only a small dependence upon the energy below the Fermi level. The X shape behavior is a consequence of the backbonds between the Ga atoms in the top dimers and the Ga atoms underneath. For very small negative voltages (0.2 eV below the VBM) only the σ-like bond of the top Ga dimer is visible [Fig. 4(g)].

The simulated STM images for unoccupied states show spots at each position of a Ga dimer of the second layer, for both the top Ga dimer [Fig. 4(h)] and the mixed dimer [Fig. 4(d)] reconstructions. In the middle of the rows there are one or two bright spots that originate from the empty dangling bonds of the topmost Ga atoms, depending on the reconstruction. The large difference between the two surface reconstructions disappears. The only difference is directly related to the replacement of a Ga atom by a P atom in the top dimer.

On comparison of the filled states results with the measured STM images described above, the agreement between the simulated mixed-dimer STM images and the experimental data lead to the conclusion that the observed reconstruction is a mixed-dimer structure. The top-Ga-dimer structure can clearly be excluded. Hence, there seems to be no structural difference between InP and GaP(001)(2×4) surface structures. Figure 5 underlines this statement. Here, the filled state STM images of the mixed-dimer reconstruction for both materials simulated at a voltage of -1.4 eV below the VBM are shown. The images for InP(001) are similar to those calculated in previous work.[13]

In summary, we have studied the STM images for filled states of the cation-rich GaP(001)(2×4) surface both experimentally and theoretically. By comparison of both types of results it has clearly been shown that the mixed-dimer reconstruction also occurs on the GaP(001) surface. A single mixed Ga-P dimer per unit cell on top of a complete Ga layer allows explanation of the observed triangular spots. Another reconstruction element such as a trimer is not necessary for explaining the observed STM images. We have also shown that the top-Ga-dimer structure, which should be stable under extreme Ga-rich conditions according to total energy calculations, does not appear for surfaces prepared as described above. Additional experiments increasing the Ga chemical potential, for example by using an extra supply of Ga, are necessary to try to prepare the most Ga-rich surface structure and to prove the theoretical predictions.

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