

Atomic structure of InP(001)-(2×4): A dimer reconstruction

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The microscopic surface structure of InP(001) is investigated by combining *first-principles* total-energy calculations with soft-x-ray photoelectron spectroscopy and scanning tunneling microscopy. The 4×2 cation dimer model adapted from Ga-rich GaAs(001) surfaces as well as recently proposed, rather complex 2×4 trimer reconstruction models are found to be unstable. The energetically favored 2×4 reconstructions are stabilized by dimerized In and P atoms. Unlike the well-known GaAs surface, however, mixed In-P dimers are preferred for cation-rich surfaces due to the notable size difference between the material constituents. [S0163-1829(98)03120-8]

The (001) surface of III-V compound semiconductors provides the growth plane for many semiconductor devices. In order to achieve a thorough understanding of its surface atomic structure a large number of experimental and theoretical studies have focused on GaAs(001). The structure of InP(001), on the other hand, is far from being understood. It has been claimed that ion bombardment and annealing of InP(001) results in a surface with an In-rich 4×2/c(8×2) reconstruction,^{1–6} in analogy to Ga-rich GaAs(001) surfaces.⁷ Recently, however, this treatment has been shown to lead to a 2×4 reconstructed surface, while the existence of a stable 4×2 reconstruction for InP(001) appears questionable.^{8,9} 2×4 reconstructions have also been found by decapping of metal-organic vapor-phase epitaxy (MOVPE) grown samples¹⁰ and by heating oxidized InP(001).¹¹ This agrees with the outcome of chemical-beam epitaxy¹² and molecular-beam epitaxy (MBE) experiments.¹³ Yang and Hasegawa¹⁴ observed a 2×4 reconstruction during gas-source MBE for both P-rich and In-rich InP(001) surfaces.

Apart from obvious contradictions concerning the translational symmetry of the reconstructed InP(001) surface, also a wide range of structural models have been suggested to explain the surface geometry. Based on high-resolution electron-energy-loss spectroscopy and ultraviolet as well as x-ray photoelectron spectroscopy, a 4×2 missing-row dimer model has been proposed, where all surface In atoms are dimerized along their dangling-bond direction and one in each four rows of In atoms is missing.^{1–3} A similar structure, known as $\beta 2(4\times 2)$ [Fig. 1(i)], is assumed to describe the ground state of Ga-rich GaAs(001) surfaces.⁷ More recently it was claimed in a series of studies that the InP surface structure cannot be explained in terms of conventional dimer models: On grounds of scanning tunneling microscopy (STM) images Shimomura *et al.*⁶ suggest a 4×2 structure that combines two In dimers in the third layer with a partial In-P exchange in the uppermost two atomic layers [Fig. 1(j)]. MacPherson and co-workers¹¹ interpret their STM images in terms of a 2×4 structure containing P trimers [Fig. 1(c)]. A 2×4 structure due to trimerization of the topmost In atoms

[Fig. 1(d)] has seemingly been observed in time-of-flight scattering and recoiling spectrometry.⁸

On the other hand, the surface optical anisotropy of 2×4 InP surfaces, which should be correlated with the surface atomic structure,¹⁵ has been shown to be almost the same for a rather wide range of preparation conditions.^{9,13,16} The existing total-energy (TE) calculations¹⁷ do not resolve the puzzle. They are limited to 4×2 reconstructions and favor the formation of P-In-P bridge bonds [Fig. 1(h)].

The present study aims at clarifying the microscopic structure of InP(001). In particular we address the question whether dimer reconstruction models are appropriate for InP surfaces or whether other reconstruction mechanisms are preferable. On the basis of STM results and core-level photoemission spectra several structural models are derived. Their total energies are then compared with the energies we calculate for surface geometries suggested in previous publications.

Our calculations are based on density-functional theory in the local-density approximation. We consider a periodic slab geometry along the surface normal. The unit cell includes an atomic slab with seven (eight) atomic InP(001) layers for cation- (anion-) terminated surfaces and a vacuum region of equivalent thickness. The cation-terminated bottom layer of the slab is saturated with fractionally ($Z=1.25$) charged H atoms. The electric field resulting from the inequivalence of the two surfaces is accounted for by a dipole correction. The electron-ion interaction is described by separable, norm-conserving pseudopotentials.¹⁸ Single-particle orbitals are expanded into plane waves up to an energy cutoff of 15 Ry. \mathbf{k} -space integrations are replaced by a sum over four special points in the irreducible part of the surface Brillouin zone (SBZ). The minimum of the TE functional with respect to both the electronic and atomic degrees of freedom is found by a molecular-dynamics approach.¹⁹ The atoms are assumed to be in relaxed positions when the forces acting on the ions are smaller than 0.025 eV/Å. The calculations are performed with the calculated equilibrium lattice constant of 5.67 Å, which is smaller than the measured value of 5.87 Å. This discrepancy is typical and remains even if temperature ef-

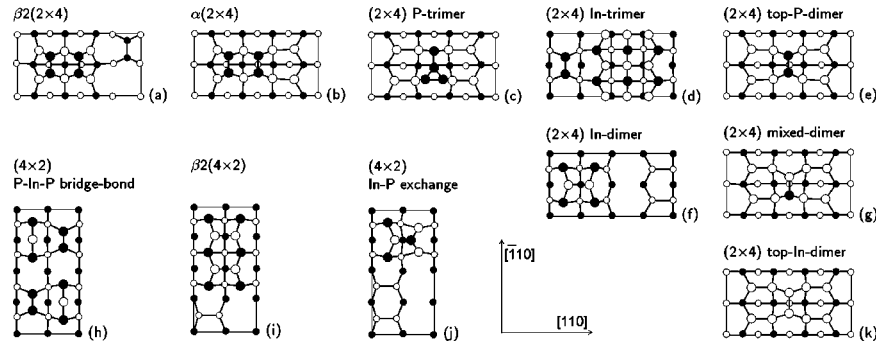


FIG. 1. Top view of relaxed InP(001)(2×4) and (4×2) surface reconstruction models. Empty (filled) circles represent In (P) atoms. Large (small) symbols indicate positions in the first and second (third and fourth) atomic layers. 2×4 and 4×2 reconstructions are ordered with increasing In coverage.

fects are taken into account. This is mainly attributed to the missing contribution of the In $4d$ states, which are considered as frozen-core states and hidden in the pseudopotential. Our approach and numerical parameters have proved reliable in determining the structural and dynamical properties of the InP(110) surface.²⁰ The calculations are on the same footing as a recent study on GaAs(001).²¹

The experimental preparation procedures have been described previously.²² The InP(001) surfaces were prepared by thermal desorption of a protective arsenic/phosphorus double layer (cap) under ultrahigh vacuum (UHV) conditions. For this purpose homoepitaxial InP epilayers were grown by MOVPE and capped *in situ* utilizing the photodecomposition of phosphine and arsine by an eximer laser source. The thermal desorption of the protective arsenic/phosphorus layer in UHV was performed by annealing to 690 K. The clean surfaces were investigated by low-energy electron diffraction (LEED), reflectance anisotropy spectroscopy, soft-x-ray photoelectron spectroscopy (SXPS), and STM. SXPS experiments were carried out at the BESSY storage ring in Berlin. The PE spectra of the In $4d$ and P $2p$ emission lines were taken in normal emission with an overall resolution of 0.2–0.25 eV using photon energies of 55 eV and 170 eV, respectively, in order to achieve optimum surface sensitivity.

The decapped InP(001) surfaces always showed clear LEED patterns with weak streaks in the twofold periodicity indicative of a coexistence of 2×4 and $c(2\times 8)$ reconstructed domains; the same reconstruction was observed on sputter/annealed and on deoxidized surfaces.^{9,11} The In $4d$ and P $2p$ emission lines obtained on the decapped surfaces are shown in Fig. 2. By line-shape analysis three components in the In $4d$ emission are deconvoluted, i.e., two surface components arise, one shifted to higher (+0.38 eV) and one shifted to lower binding energy (BE) (−0.43 eV). After prolonged annealing, on sputter/annealed and on deoxidized surfaces an additional fourth In component due to metallic In shows up (not shown here). In the P $2p$ emission lines, on the other hand, only two components are deconvoluted, i.e., one surface component appears, shifted to lower BE (−0.36 eV). The In $4d$ at higher and the P $2p$ surface component at lower BE, respectively, are most likely due to the charge transfer from indium to phosphorous surface atoms as postulated by the electron counting rule.²³ Accordingly, In atoms with one empty and P atoms with one doubly occupied dangling bond should exist at the surface. The low-BE surface component

of In $4d$ indicates the presence of another In surface bonding site, which is characterized by a relative charge accumulation with respect to the phosphorous-coordinated bulk indium. Similar photoemission spectra have been reported in case of the Ga-rich GaAs(001)-(4×2) reconstruction: low-BE and high-BE surface components of Ga $3d$ and only one low-BE component of As $3d$.²⁴ Thus our SXPS results strongly suggest an In-rich surface structure complying with the electron counting rule.

Atomically resolved STM images of the decapped InP surface show 2×4 and $c(2\times 8)$ reconstructed domains (cf. Ref. 10), in agreement with the LEED pattern. The STM images of the reconstructed InP surface are, however, clearly different from those of the well-studied, As-dimer-terminated GaAs(001)-(2×4) surface. In the case of GaAs one half of the row consists of two As dimers, the other half to the two adjacent missing dimers. For InP the elevated part is considerably smaller than one-half of the row.¹⁰ An InP surface structure constructed of two P dimers next to two missing dimers (in analogy to the As-terminated 2×4 GaAs surface) would not fit the STM pattern. Furthermore, the domain boundaries reported in Refs. 6 and 11 cannot be explained in terms of the dimer models known from GaAs(001).

In order to explain the experimental findings we performed TE calculations for eleven different 2×4 and 4×2

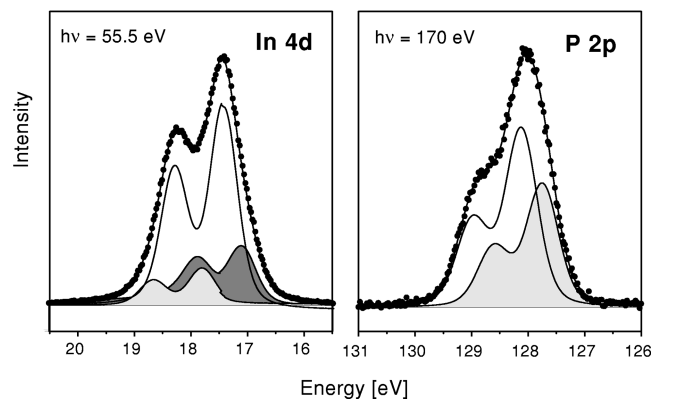


FIG. 2. Deconvolution of SXPS spectra of the P $2p$ and In $4d$ core level emission into surface (shaded) and bulk (light) components. Each component consists of a spin-orbit-split doublet. Two surface components of the In $4d$ and one surface component of the P $2p$ emission arise.

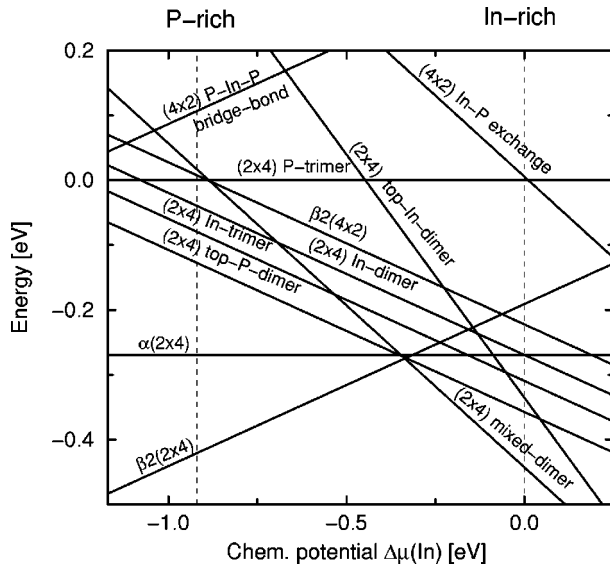


FIG. 3. Relative formation energy (with respect to the P-trimer structure) per 1×1 unit cell for InP(001) surface reconstructions vs $\Delta\mu(\text{In}) = \mu_{\text{bulk}}(\text{In}) - \mu(\text{In})$. The thermodynamically allowed range $-\Delta H_f(\text{InP}) [= 0.92 \text{ eV (Ref. 28)}] \leq \Delta\mu(\text{In}) \leq 0$ is indicated by dashed lines.

surface reconstruction models. Four of them are novel structures [Figs. 1(e), 1(f), 1(g), and 1(k)]; the others have either been suggested in earlier publications^{11,8,17,6} [Figs. 1(c), 1(d), 1(h), and 1(j)] or have been adapted from GaAs(001) [Figs. 1(a), 1(b), 1(i)].^{7,21,25} The four structures that we propose are consistent with the STM and SXPS data: (i) They contain single dimers in the top layer orientated along the $[110]$ (In dimer model) or $[\bar{1}10]$ direction (top-P-dimer, mixed-dimer, and top-In-dimer model) in order to account for the rather narrow protrusions observed by STM; (ii) they have 2×4 unit cells, in agreement with the observed translational symmetry; (iii) they correspond to In-rich surfaces as suggested by the SXPS results; and (iv) they contain two differently coordinated surface In atoms, which could account for the finding of three In $4d$ components. The formation of In-In bonds between threefold- and fourfold-coordinated surface cations would explain the experimental observation of low- and high-BE components by means of simple charge-transfer arguments.

The structures considered in the TE calculations realize different In coverages of $\Theta = 1/4$ [$\beta 2(2 \times 4)$, P-In-P bridge bond], $\Theta = 1/2$ (α , P trimer), $\Theta = 3/4$ [$\beta 2(4 \times 2)$, In trimer, In dimer, top P dimer], $\Theta = 1$ (In-P exchange, mixed dimer), and $\Theta = 5/4$ (top In dimer).²⁶ Therefore, an energetic comparison of these structures can only be made by taking into account the chemical potentials of the surface constituents In and P (for details see, e.g., Ref. 27). In Fig. 3 we show the relative formation energies of the surface structures vs the allowed range of the In chemical potential.

For In-rich surfaces our calculations favor clearly the formation of mixed In-P dimers on top of an In-terminated surface [Fig. 1(g)]. This structure would also explain the experimental findings by SXPS and STM: One P $2p$ vs two In $4d$ surface components reflect the singular P-surface site vs two distinct In-surface sites (threefold and fourfold coordination). Even more convincing, the asymmetry in the structural units

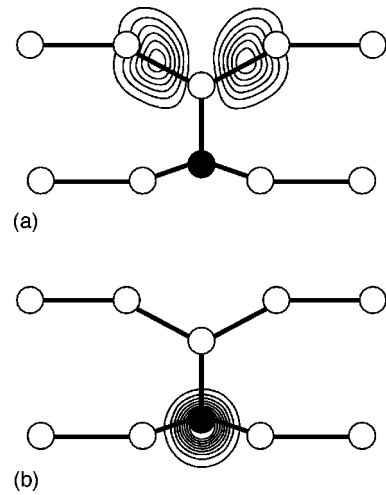


FIG. 4. Contour plots of the squared wave functions at K for the two highest occupied surface states (a) V1 and (b) V2 of the mixed-dimer model. The contour spacing is $10^{-3} \text{ bohr}^{-3}$. The plots for V1 and V2 are drawn in (001) planes 0.8 \AA below and 0.8 \AA above the uppermost P atom, respectively. The lateral positions of the uppermost In (P) atoms are indicated by empty (filled) circles.

found by STM at low negative bias voltages^{6,11} would readily be explained by the asymmetric surface dimers. This is substantiated by our electronic structure calculations: Pronounced occupied surface bands occur only around the K point of the SBZ. The two highest occupied surface states V1 and V2 have energies 0.1 and 0.4 eV below the bulk valence band edge at K . They are related to σ -like bonds between the top In atom and the two cations below and to a dangling bond located at the top P atom, respectively (cf. Fig. 4). The lateral positions of the resulting three maxima in the electron density due to these states form an isosceles triangle, in excellent agreement with the measured corrugation. Furthermore, the observed domain boundaries^{6,11} can easily be constructed by means of asymmetric single dimer units and the bonding geometry of the second-layer In atoms below the topmost dimers fits very well the “zipperlike” rows reported in Ref. 11.

For less-In-rich surfaces our calculations indicate the stability of the $\beta 2(2 \times 4)$ reconstruction adapted from As-rich GaAs surfaces.^{21,25} This agrees with the observation of two different 2×4 phases.^{13,14} Taking the limited accuracy of our calculations into account, however, we cannot exclude the existence of further surface structures for a very narrow range of preparation conditions: The $\alpha(2 \times 4)$ phase as hypothesized in Ref. 13 and/or the top-P-dimer geometry may occur for intermediate values of the In chemical potential. For P-rich surfaces, on the other hand, 2×1 , 2×2 , and $c(4 \times 4)$ reflection high-energy electron-diffraction patterns have been observed.¹³ Therefore, geometries other than those included in the present study may be favored for very P-rich conditions.

The energetically most favorable 4×2 reconstruction, the InP(001) $\beta 2(4 \times 2)$ structure, is about 0.14 eV per surface atom higher in energy than the 2×4 top-P-dimer model. Therefore, it can safely be excluded to be an equilibrium structure. It is interesting to note that the only model that does not satisfy electron counting heuristics,²³ namely, the

P-In-P bridge-bond model,¹⁷ is among the most unfavorable geometries. This indicates the validity of the electron counting rule for InP(001) surfaces. The trimerlike surface structures suggested in Refs. 8 and 11 as well as the In-P exchange⁶ are also significantly higher in energy than dimer reconstruction models and thus can be ruled out.

The mixed-dimer phase of In-rich surfaces has no counterpart at the well investigated GaAs(001) surface.^{7,21,25} In the latter case the Ga-rich surface is characterized by the $\beta 2(4 \times 2)$ structure, where three surface cation dimers orientated along [110] form the 4×2 surface unit cell. An explanation for the energetic preference of isolated dimers for InP surfaces is the relatively low subsurface strain, while at the same time the electron counting rule can be fulfilled. The large size difference between anions and cations in the case of InP hinders the accommodation of sp^2 -hybridized In-dimer atoms [as in case of the $\beta 2(4 \times 2)$ structure] at the surface due to an appreciable stress in the subsurface layers caused by the threefold-coordinated cations. The mixed-dimer model, on the other hand, allows the formation of

strong In-In bonds (bond lengths 2.7–2.9 Å) while, due to the fact that four surface In atoms remain fourfold coordinated and near their ideal positions, the surface stress is low. The same arguments hold in the case of α and top-P-dimer structures, which may occur for a small range of preparation conditions.

In conclusion, we have presented a comprehensive study of the energetics of 2×4 and 4×2 reconstructions of InP(001) combined with core-level photoemission and STM experiments. Both for a balanced surface stoichiometry and for In-rich conditions we favor a 2×4 reconstructed surface that is stabilized by the formation of dimers. The cation-rich surface contains mixed In-P dimers, unlike the well-investigated GaAs(001) surface, which is attributed to the remarkable size difference between cations and anions in InP. Our results explain naturally all the recent experimental findings.

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