InP(001)-(2 × 1) Surface: A Hydrogen Stabilized Structure

W. G. Schmidt,* P. H. Hahn, and F. Bechstedt

Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, Max-Wien-Platz 1, 07743 Jena, Germany

N. Esser, P. Vogt, A. Wange, and W. Richter

Institut für Festkörperphysik, Sekretariat PN 6-1, TU Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

The InP(001)(2 × 1) surface has been reported to consist of a semiconducting monolayer of buckled phosphorus dimers. This apparent violation of the electron counting principle was explained by effects of strong electron correlation. Combining *first-principles* calculations with reflectance anisotropy spectroscopy and LEED experiments, we find that the (2 × 1) reconstruction is not at all a clean surface: it is induced by hydrogen adsorbed in an alternating sequence on the buckled P dimers. Thus, the microscopic structure of the InP growth plane relevant to standard gas phase epitaxy conditions is resolved and shown to obey the electron counting rule.

In the last few decades intensive research has focused on semiconductor surface structures [1]. On the one hand, the forces driving the surface structure formation are important for the understanding and control of material growth at a microscopic level. Usually, however, the surface structures formed in the technologically relevant gas phase epitaxy are not known in detail, but are simply assumed to be similar to those of the clean surface in ultrahigh vacuum (UHV) [2]. On the other hand, semiconductor surfaces allow for the two-dimensional or even one-dimensional confinement of electrons, thus giving rise to peculiar many-body effects which are of fundamental interest. Recent examples include the Mott-Hubbard insulating behavior of the SiC(0001)($\sqrt{3} \times \sqrt{3}$) surface [3], or the phase transitions in one-dimensional metallic chains on silicon substrates (see, e.g., Ref. [4]).

The electronic and structural properties of III-V compound (001) surface reconstructions, by contrast, are generally believed to be governed by a few simple principles [1,5]. (i) The exposed surface atoms form dimers 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 [6]. (iii) The resulting combination of dimers and missing dimers is arranged in such a way that the surface Madelung energy is minimized [5,7].

Recent works on the nominal (2 × 1) reconstructed, P-rich InP(001) surface, however, indicate that this system may be an exception from the above rules and can be understood only by invoking many-body effects. From a variety of surface analysis results it was consistently concluded that under specific preparation conditions one complete monolayer of buckled phosphorus dimers is formed [8,9]. Zigzag chains were clearly resolved by scanning tunneling microscopy (STM) [8,9] and photoemission spectra showed two inequivalent P-adsorption

sites [9]. Such a structure necessarily violates the electron counting principle and should be metallic [6]. However, a surface energy gap between valence and conduction states of more than 1 eV was measured by scanning tunneling spectroscopy [8]. In order to explain this striking contradiction, the opening of a Mott-Hubbard gap due to strong electron correlation effects across the dimer rows was suggested [8,10]. It was proposed that the P dimers buckle as a result of the electron correlation and form zigzag chains along the [110] direction.

Interestingly, well-ordered (2 × 1) surface structures have exclusively been observed by groups using metal organic vapor phase epitaxy (MOVPE) and chemical beam epitaxy (CBE) [8–12]. As known from reflectance anisotropy spectroscopy (RAS) and electron diffraction studies, the (2 × 1) structure is present under standard growth conditions in MOVPE and CBE. In molecular beam epitaxy (MBE), to the contrary, a disordered surface, sometimes referred to as (2 × 1)-like, is formed under P-rich conditions [13,14]. An extensive computational search for geometries able to explain the peculiar (2 × 1) surface ordering failed [15]. Symmetric, rather than asymmetric, P dimers were found to be energetically favored.

While hydrogen is present in MOVPE and CBE, it is absent under MBE conditions. Furthermore, hydrogen is difficult to detect. It may thus be the key to resolve the puzzle of the (2 × 1) surface. In this Letter we therefore explore the possibility that the well-ordered (2 × 1) surface is a hydrogen-adsorbate structure, rather than a clean InP(001) surface stabilized by strong electron correlation. By means of *first-principles* calculations we identify an energetically favored, hydrogen-stabilized surface which accounts well for all available experimental findings. A direct experimental proof for the hydrogen-induced (2 × 1) reconstruction is given by performing RAS and low energy electron diffraction (LEED) experiments in MBE using an additional source of atomic hydrogen.

Our calculations are based on a massively parallel, real-space finite-difference implementation [16] of the density-functional theory in the local-density approximation (DFT-LDA). A multigrid technique is employed for convergence acceleration. The computational details are like those in Ref. [5]. We investigate more than 50 plausible structures which differ with respect to their geometries, their In/P ratio, and the number of adsorbed hydrogen atoms. The energetically favored hydrogen-induced surface reconstructions are shown in Fig. 1 [17].

Because of the varying surface stoichiometry, the total energies of the investigated structures cannot directly be used to determine the surface ground state. Rather, the thermodynamic grand-canonical potential Ω with dependence on the chemical potentials μ of In, P, and H needs to be considered [18]. Since the surface is in equilibrium with the bulk compound, $\mu(\text{In})$ and $\mu(\text{P})$ are related to each other: their sum equals the chemical potential of bulk InP. Consequently, the surface formation energy may be written as a function of only two variables, which we take to be the relative chemical potential of the cation with respect to its bulk phase, $\Delta\mu(\text{In})$, and the chemical potential of hydrogen with respect to its molecular phase, $\Delta\mu(\text{H})$. The computational accuracy in determining the chemical potentials is of the order of 0.1 eV [19].

The resulting phase diagram in dependence upon the chemical potentials of In and H is shown in Fig. 2. Here $\Delta\mu(\text{H}) = 0$ 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 $\Delta\mu(\text{H})$ can be approximated by that of a two-atomic ideal gas. A hydrogen chemical potential $\Delta\mu(\text{H})$ of about -1 eV is estimated to correspond to typical MOVPE growth conditions [20]. If no hydrogen is present, i.e., for $\Delta\mu(\text{H}) \ll 0$, InP forms the surface reconstructions typical for the clean surface [5]. The structures stable for $\Delta\mu(\text{H}) > 0$ may form if atomic hydrogen is available.

Two general trends are revealed by the total-energy calculations. (i) Hydrogen is more likely to bond to surface P atoms than to surface In. This is related to the high electronegativity of H, rendering the attachment to P lone pairs favorable. (ii) H adsorption occurs mainly at the uppermost atomic layer, even if bonding sites in the layer beneath are available. This trend may contribute to the H-induced long-range ordering of the InP surface as opposed to an immediate destruction, such as commonly observed for other III-V(001) surfaces.

The (2×2)-2D-2H surface, i.e., the periodic arrangement of oppositely buckled ($\Delta z = 0.30$ Å) P dimers on top of an In-terminated substrate, is very dominant in the surface phase diagram. One H atom is bonded to the
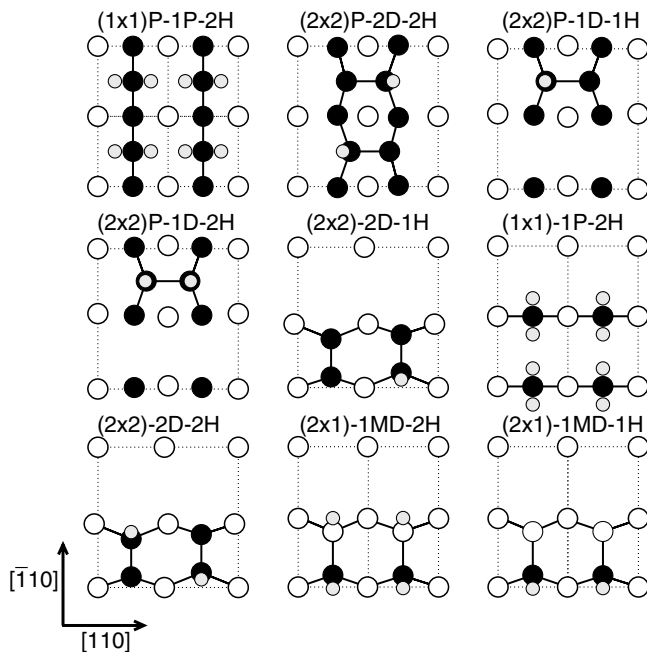

FIG. 1. Top view of relaxed InP(001):H surface structures [17]. Empty (filled, grey) circles represent In (P, H) atoms. The surface unit cells are indicated.
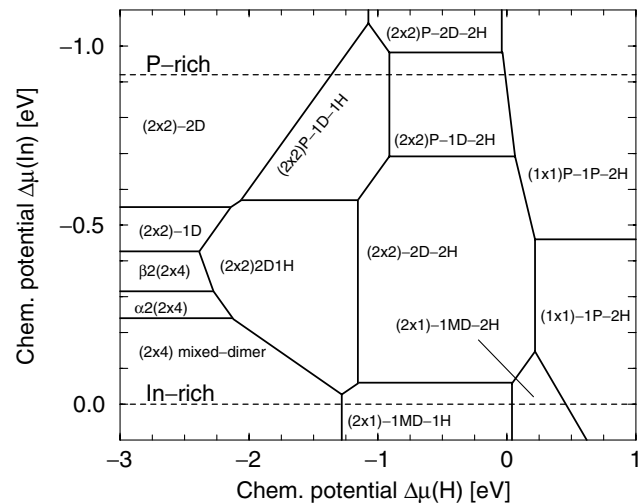

FIG. 2. Calculated phase diagram of the hydrogen exposed InP(001) surface. Dashed lines indicate the approximate range of the thermodynamically allowed values of $\Delta\mu(\text{In})$. The chemical potential of hydrogen, $\Delta\mu(\text{H})$, is given with respect to molecular hydrogen.

"down" atom of the P dimer. This structure should form for moderately P-rich to In-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 MOVPE- or CBE-grown InP(001) samples. However, energy arguments alone are not sufficient to establish the correspondence between the 2D-2H structure and the well-ordered (2×1) surface. Its formation may be kinetically hindered. Therefore we compare in the following the spectroscopic properties of the 2D-2H structure with the available experimental findings.

(i) The structure obeys the electron counting principle. We calculate a DFT-LDA surface band gap of 0.75 eV. This value is lower than the one measured for the zigzag chain structure of 1.2 ± 0.2 eV [8]. The discrepancy, however, is due to the failure of density-functional calculations to correctly describe excited states. Quasiparticle effects open the InP(001) surface band gap calculated within DFT-LDA by about 0.4–0.5 eV [21]. The 2D-2H model, therefore, accounts very well for the scanning tunneling spectroscopy findings.

(ii) The STM image of the buckled-dimer structure, calculated according to the Tersoff-Hamann approach [22], is shown in Fig. 3. A bias voltage of -5 eV was used to allow for a comparison with the experimental data. Clearly, the simulated STM image is in very good agreement with the measured images in Refs. [8,9]. The bright spots visible in the image are due mainly to the lone pair at the "up" atom of the P dimer, forming the highest occupied surface state. The energetically

well separated hydrogen bond at the down atom explains why only one P atom is seen in the STM experiment.

(iii) RAS is particularly suitable for surface structure exploration during epitaxial growth [2,11]. In contrast to other surface analysis techniques, it allows for a direct comparison between surfaces in UHV and in gas phase epitaxy conditions. In Fig. 4 the RAS spectrum calculated [24] for the (2×2)-2D-2H structure is compared with the optical anisotropy measured for the MOVPE-prepared InP(001)(2×1) surface [23]. The calculation reproduces well the minimum/maximum structure characteristic for MOVPE- or CBE-grown samples [9,11,23]. The slight deviations which occur with respect to the energy positions and magnitudes of the optical anisotropy are to be expected, because in the calculations we approximate self-energy effects by the scissors-operator approach [25] and completely neglect excitonic and local-field effects [26] as well as the influence of surface defects. Obviously, the 2D-2H structure favored from total-energy calculation explains very well all experimental findings available for the well-ordered InP(001)(2×1) surface.

In order to prove that indeed the adsorption of hydrogen is responsible for the formation of the ordered (2×1) surface, we directly investigate its influence on the MBE-prepared InP(001) surface. We perform RAS and LEED experiments on homoepitaxially grown layers with and without *in situ* exposure to atomic hydrogen. In Fig. 4 the RAS spectrum measured for the MBE-grown
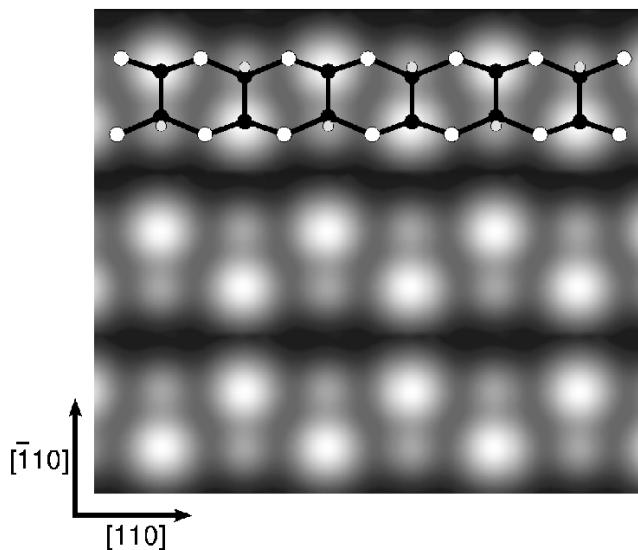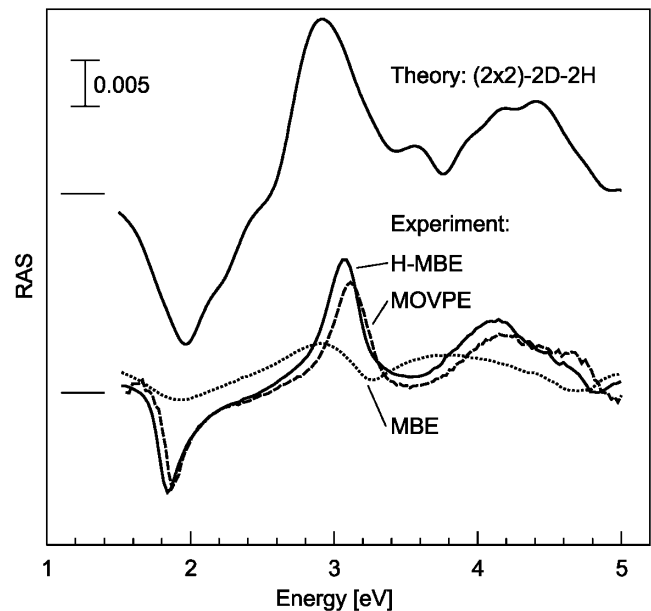

FIG. 3. Calculated STM image of the P monolayer-terminated InP(001) surface, consisting of oppositely buckled dimers, with hydrogen attached to the "down" atom. A phase shift between the dimer rows allows for (2×2) and $c(4 \times 2)$ reconstructed domains.

FIG. 4. RAS spectra $[\mathrm{Re}\{(r_{[1\bar{1}0]} - r_{[110]})/\langle r \rangle\}]$ measured for P-terminated InP(001)(2×1) surfaces prepared by MBE, by MBE with additional hydrogen supply, and by MOVPE (from Ref. [23]) are compared with the spectrum calculated for the InP(001)(2×2)-2D-2H structure (cf. Fig. 1).

(2×1)-like surface is shown. This spectrum is typical for a wide range of preparation conditions, with the P_2 partial pressure ranging from 5×10^{-8} to 3×10^{-3} mbar and the substrate temperature ranging from room temperature to 730 K. It does not show any strong minimum/maximum features. The optical anisotropy is weak and residual features refer to the E_1 and $E_1 + \Delta_1$ bulk critical points [21]. Consistent with earlier STM work [13], the RAS spectrum and the diffuse LEED pattern in our experiment demonstrate that the MBE-prepared (2×1)-like surface does not have long-range periodicity. The surface optical anisotropy changes drastically, however, as soon as atomic hydrogen is dosed together with P_2 after MBE growth of a homoepitaxial P layer. The corresponding RAS spectrum (denoted H-MBE in Fig. 4) is almost identical to the one typical for MOVPE-grown samples, showing the characteristic minimum/maximum structure. The LEED measurements for this surface display the $(2 \times 1)/(2 \times 2)$ pattern typical for MOVPE-prepared samples [9]. The experiment thus shows that the well-ordered (2×1) surface is formed only in the presence of hydrogen. From the comparison of the measured RAS spectra we can conclude that the surface structure corresponds to the one obtained under MOVPE and CBE conditions. The comparison with the results of the *first-principles* calculations, finally, allows for identifying this structure with the 2D-2H model.

In conclusion, we have demonstrated that the well-ordered (2×1) reconstruction of the InP(001) 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 InP(001):H structure derived here. No effects of strong electron correlation need to be invoked in order to understand the experiments. The 2D-2H model complies with the electron counting rule. Our work underlines the influence of adsorbates resulting from the decomposition products of precursors on the microscopic surface structure during MOVPE and CBE growth.

*Electronic address: W.G.Schmidt@ifto.physik.uni-jena.de

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