

SURFACE ORDERING OF P-RICH InP(001): HYDROGEN STABILIZATION VS ELECTRON CORRELATION

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The influence of hydrogen on the reconstruction of InP(001) surfaces is studied by *first-principles* calculations. One-monolayer phosphorus forming oppositely buckled dimers with one hydrogen adsorbed per dimer is energetically favored for a wide range of surface preparation conditions. The electronic structure and STM image calculated for this adsorbate geometry agree well with the experimental findings obtained after annealing of MOVPE-grown InP samples. The Si(001)-like surface ordering as well as the surface band gap of more than 1 eV, supposedly arising from electron correlation effects [Li *et al.*, *Phys. Rev. Lett.* **82**, 1879 (1999)], are naturally explained by the hydrogen-stabilized surface structure favored by the total-energy calculations.

1. Introduction

The ideal III-V(001) surface is polar, being terminated either entirely by cations or anions. However, such an ideal termination is usually not observed.^{1–3} InP(001) seems to be a remarkable exception in that respect. For specific P-rich preparation conditions it is apparently terminated by a complete phosphorus monolayer.^{4,5} Such a structure clearly violates the electron counting rule⁶ and should be metallic. However, in this case an energy gap between valence and conduction states of more than 1 eV was measured. The formation of this unusual surface structure and the band gap were explained by strong electron correlation effects across the dimer rows between the P dangling bonds.⁴ As a result, the P dimers buckle and form zigzag chains along the [110] direction. Zigzag chains are indeed clearly resolved by STM.^{4,5} Depending on whether two adjacent chains are in or out of phase, (2×2) - and $c(4 \times 2)$ -reconstructed domains, reminiscent of the Si(001) surface, are observed.

Such observations, however, have exclusively been made by groups using metal-organic vapor phase epitaxy (MOVPE) to prepare their InP samples.^{4,5} Samples prepared by molecular beam epitaxy (MBE) show only two reconstructions with long range periodicity, $c(4 \times 4)$ and (2×4) .^{7,8} On the other hand, to our knowledge the $c(4 \times 4)$ surface

has never been observed on gas-source grown samples.^{4,5,9–11} The MBE results agree with total-energy calculations,³ which identified several stable surface geometries with (2×4) and $c(4 \times 4)$ periodicity. On the other hand, an extensive computational search¹² for geometries able to explain the peculiar, Si(001)-like surface ordering failed to explain the MOVPE findings.^{4,5} Symmetric rather than asymmetric P dimers were found to be energetically favored.

A solution of this puzzle is highly desirable: MOVPE is an essential technology for manufacturing compound semiconductor devices, in particular those containing phosphide-based materials. The microscopic understanding of surfaces prepared from MOVPE-grown samples is the prerequisite for any reliable computational modeling of the complex transport and reaction phenomena during the epitaxial growth. In the present study we explore the possibility that the apparent discrepancies between the outcome of MOVPE and MBE experiments can be explained by the presence of hydrogen in the former case.

2. Computational Method

Our calculations are based on a massively parallel, real-space finite-difference implementation¹³ of the density-functional theory in the local-density

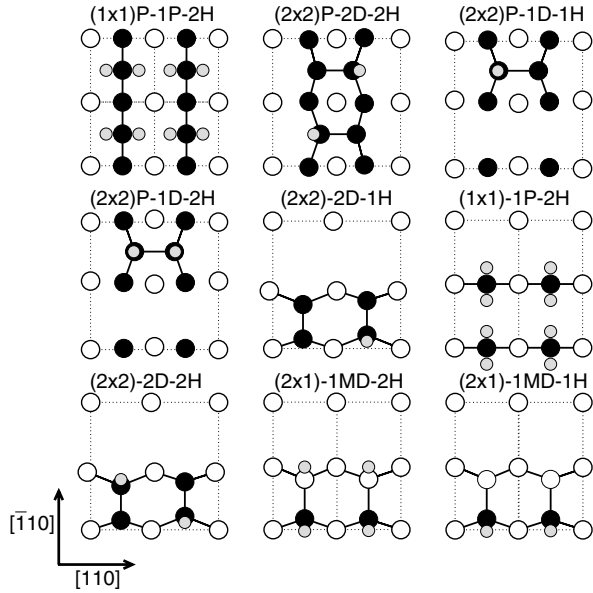


Fig. 1. Top view of relaxed InP(001): H surface structures. Empty (filled, gray) circles represent In (P, H) atoms. The surface unit cells are indicated.

approximation (DFT-LDA). A multigrid technique is employed for convergence acceleration. The surfaces are modeled using periodic supercells. They contain material slabs of 16 InP(001) layers, separated by the equivalent of 10 atomic layers of vacuum. The cation-terminated bottom layer of the slab is saturated with fractionally ($Z = 1.25$) charged pseudohydrogen.¹⁴ The bottom two atomic layers are kept frozen, whereas all remaining atoms are allowed to relax. Further computational details are like those in Ref. 3.

The possibility of hydrogen adsorption leads to a large number of conceivable surface structures. We investigate more than 50 different 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. The notation of surface structures is chosen 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 In-P dimers, respectively. The number of hydrogens per surface unit cell concludes the notation.

Due to the varying surface stoichiometry, the total energies of the studied structures cannot directly be used to determine the surface ground state.

Rather, the thermodynamic grand-canonical potential Ω in dependence on the chemical potentials μ of In, P and H needs to be considered.¹⁵ Since the surface is in equilibrium with the bulk compound, μ_{In} and μ_{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 indium with respect to its bulk phase and the chemical potential of hydrogen with respect to its molecular phase. The computational accuracy in determining the chemical potentials is of the order of 0.1 eV.¹⁶ From convergence tests, the uncertainty of the calculated surface energies is estimated to be about than 0.01 eV per surface atom.

3. Results

The calculated surface phase diagram, in terms of its dependence on the chemical potentials of In and H, is shown in Fig. 2. Here zero hydrogen chemical potential corresponds to the situation where the surface is exposed to molecular hydrogen at $T = 0$ K. For higher temperatures the surface phase diagram will change, due to vibrational contributions to the energy and entropy of the surface structures, and due to the temperature (and pressure) dependence of the

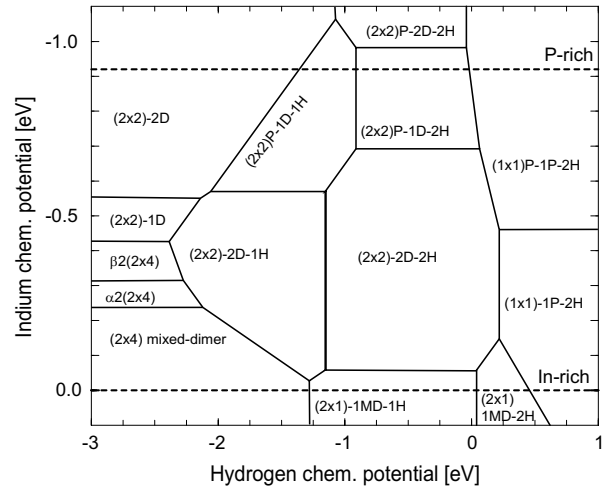


Fig. 2. Calculated phase diagram of the hydrogen-exposed InP(001) surface. Dashed lines indicate the approximate range of the thermodynamically allowed values of the In chemical potential. The chemical potential of hydrogen is given with respect to molecular hydrogen at $T = 0$ K.

chemical potentials of the surface constituents. By far the largest change of the surface energetics, however, 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.^{17,18}

$$\Delta\mu_{\text{H}}(T) = \frac{1}{2} kT \left[\ln \left(\frac{p\lambda^3}{kT} \right) - \ln Z_{\text{rot}} - \ln Z_{\text{vib}} \right], \quad (1)$$

where k is the Boltzmann constant, T the temperature, p the pressure, $\lambda = \left(\frac{h^2}{2\pi mkT} \right)^{1/2}$ the de Broglie thermal wavelength of the H_2 molecule, and Z_{rot} and Z_{vib} its rotational and vibrational partition functions, respectively. By increasing the temperature, the hydrogen chemical potential is lowered, i.e. less energy is gained by taking a H atom out of the reservoir and attaching it to the InP surface. In Fig. 3 we show the temperature and pressure values corresponding to specific values for $\Delta\mu_{\text{H}}(T)$. A hydrogen chemical potential $\Delta\mu_{\text{H}}$ of about -1 eV can be estimated to correspond to typical MOVPE growth conditions.

The structures indicated for $\Delta\mu_{\text{H}} > 0$ in the phase diagram of Fig. 2 may form when atomic hydrogen becomes available for the surface reaction. In that case the reaction barrier is also substantially lowered. If no hydrogen is present, i.e. for $\Delta\mu_{\text{H}} \ll 0$, InP forms the surface reconstructions typical for the clean surface.³ The $c(4 \times 4)$ reconstruction, not visible in the present phase diagram, is energetically nearly degenerate with other P-rich surface reconstructions. It is stable for a narrow range of $\Delta\mu_{\text{In}}$ between the (2×2) -2D and (2×2) -1D surfaces.

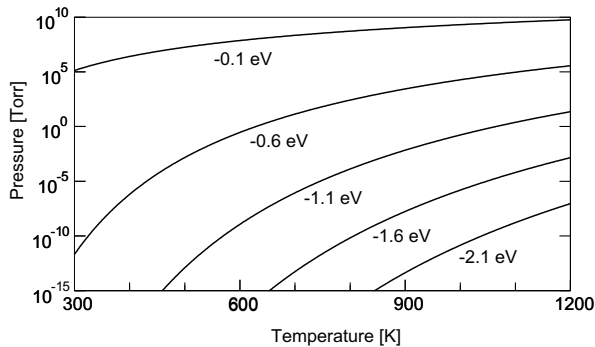


Fig. 3. Temperature and pressure values corresponding to given relative change of the hydrogen chemical potential with respect to its molecular value at $T = 0$ K.

As one expects, the higher the value of the hydrogen chemical potential, the more H atoms adsorb on the surface. In addition, two less obvious trends are revealed by the calculations:

- (i) Hydrogen is more likely to bond to surface P atoms compared to surface In. That 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, as commonly observed for other III-V(001) surfaces.

The (2×2) -2D-2H surface is the most dominant structure in the calculated surface phase diagram in Fig. 2. It should occur for a wide range of surface preparation conditions. It is formed by a periodic arrangement of oppositely buckled ($\Delta z = 0.30$ Å) P dimers on top of an In-terminated substrate. One H atom is bonded to the “down” atom of the P dimer (cf. Fig. 1). While this structure seems to represent the surface ground state for annealed MOVPE-grown InP(001) surfaces, energetical arguments alone are only an indication that this structure indeed corresponds to the surface observed experimentally,^{4,5} because its formation may be kinetically hindered.

In order to clarify whether the 2D-2H structure indeed corresponds to the experimental observations, we investigate its electronic structure. 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. 4. The surface band gap calculated in DFT-LDA amounts to 0.75 eV. This value is lower than the one measured for the zigzag chain structure of 1.2 ± 0.2 eV.⁴ This discrepancy, however, can be explained by the insufficient description of the electronic self-energy within the DFT-LDA, i.e. the DFT-LDA band gap problem.¹⁹ The inclusion of quasiparticle effects results in an opening of the InP(001) surface band gap by about 0.4–0.5 eV.²⁰

The highest occupied surface band, V1, is due to the dangling bonds on the “up” atoms of the phosphorus dimers. The lowest unoccupied surface band, C1, is related to an antibonding σ^* combination of in-plane p orbitals localized at the P dimer atoms (cf. Fig. 5).

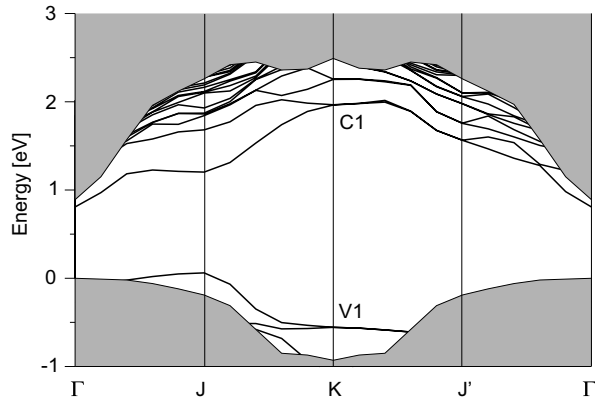


Fig. 4. Surface band structure for the (2×2) -2D-2H surface. Gray regions indicate the projected bulk band structure.

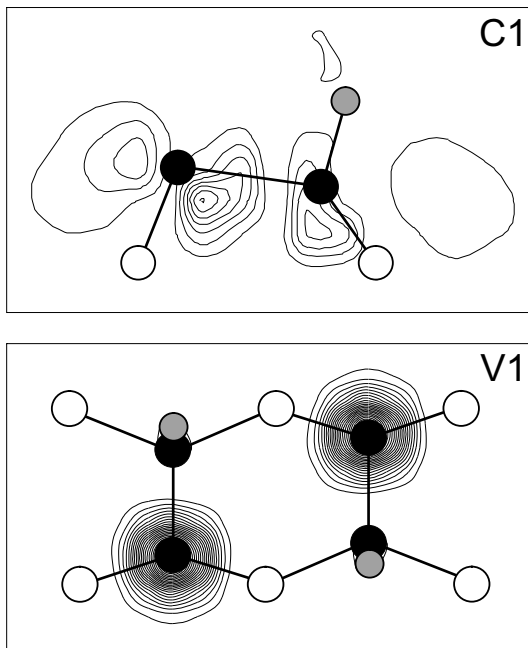


Fig. 5. Contour plots of the squared wave functions of the (2×2) -2D-2H surface at the K point of the (2×2) surface Brillouin zone. Top and side views are given for V1 and C1, respectively.

In Fig. 6 we show an STM image of the (2×2) -2D-2H surface, calculated according to the Tersoff–Hamann approach.²¹ A bias voltage of -5 eV was used, to allow a comparison with the experimental data.^{4,5} Clearly, the simulated STM image is in very good agreement with the measured data (cf. e.g., Fig. 2 of Ref. 4). The bright spots visible in the image are due mainly to the dangling bonds at the “up” atom of the P dimer, i.e. the V1 surface state. The

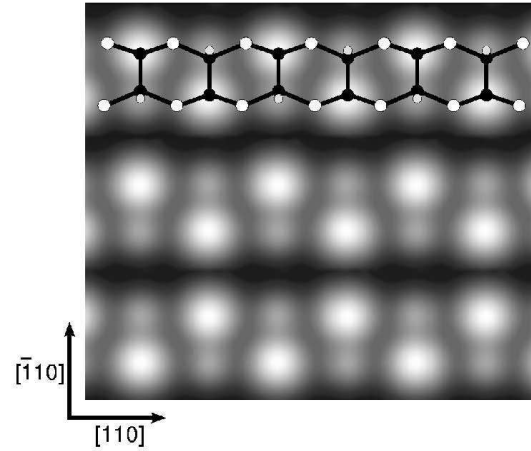


Fig. 6. STM image calculated for the (2×2) -2D-2H surface.

alternating arrangement of the dangling bond causes the appearance of zigzag chains in the STM. By varying the phase shift between adjacent zigzag chains, the observation of (2×2) - and $c(4 \times 2)$ -reconstructed domains can be explained.

We mention that experimental evidence for the existence of hydrogen at annealed, MOVPE-grown InP(001) (2×1) surfaces has recently been obtained by optical spectroscopy.²²

The calculated phase diagram also explains the experimental finding of a poorly ordered, even more P-rich surface formed on samples immediately after the MOVPE growth (i.e. without annealing procedures). STM images of such surfaces^{5,9} show oval features arranged with local (2×2) , $c(2 \times 2)$ and $c(4 \times 2)$ symmetry. For P- and H-rich surfaces, the (2×2) P-1D-2H structure is stable. It corresponds to the adsorption of two H atoms on single P dimers on top of a P-terminated substrate. The simulated STM image for this H-saturated dimer (not shown here) resembles the oval shapes observed experimentally.^{5,9} The (2×2) P-1D-2H structure is energetically nearly degenerate with (1×2) and $c(2 \times 2)$ surface reconstructions, featuring P dimers saturated with two H atoms on top of a P monolayer. This energetic degeneracy explains the disorder typical for MOVPE-grown samples terminated with more than one monolayer of phosphorus.

4. Conclusions

In conclusion, we performed *first-principles* total-energy calculations for a large variety of clean and

H-covered InP(001) surfaces. Oppositely buckled P dimers with one hydrogen adsorbed are energetically favored for a wide range of the surface chemical potentials. The simulated STM image as well as the calculated surface band gap for this structure agree very well with the experimental findings obtained for P monolayer-terminated InP(001) surfaces prepared by the annealing of MOVPE-grown samples. The adsorption of hydrogen thus provides a simple explanation, as opposed to electron-correlation effects, for the experimental observation of a Si(001)-like surface ordering and the existence of a band gap. Our results underline the strong influence of the surface preparation procedures on the geometries finally obtained.

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