

P-Terminated InP (001) Surfaces: Surface Band Bending and Reactivity to Water

Dominik Christian Moritz, Isaac Azahel Ruiz Alvarado, Mohammad Amin Zare Pour, Agnieszka Paszuk, Tilo Frieß, Erich Runge, Jan P. Hofmann, Thomas Hannappel, Wolf Gero Schmidt,* and Wolfram Jaegermann*



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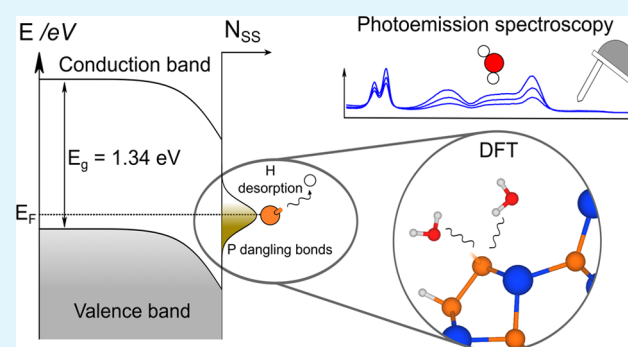
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ABSTRACT: Stable InP (001) surfaces are characterized by fully occupied and empty surface states close to the bulk valence and conduction band edges, respectively. The present photoemission data show, however, a surface Fermi level pinning only slightly below the midgap energy which gives rise to an appreciable surface band bending. By means of density functional theory calculations, it is shown that this apparent discrepancy is due to surface defects that form at finite temperature. In particular, the desorption of hydrogen from metalorganic vapor phase epitaxy grown P-rich InP (001) surfaces exposes partially filled P dangling bonds that give rise to band gap states. These defects are investigated with respect to surface reactivity in contact with molecular water by low-temperature water adsorption experiments using photoemission spectroscopy and are compared to our computational results. Interestingly, these hydrogen-related gap states are robust with respect to water adsorption, provided that water does not dissociate. Because significant water dissociation is expected to occur at steps rather than terraces, surface band bending of a flat InP (001) surface is not affected by water exposure.

KEYWORDS: InP, Fermi level pinning, band bending, water adsorption, P-rich, dangling bond defect, surface reactivity



1. INTRODUCTION

Because of their promising photovoltaic performance, III–V photoabsorbers such as InP have gained a lot of attention with respect to their application in the field of photoelectrochemical water splitting.^{1,2} As a benchmark system for binary III–V semiconductors, InP can be prepared either In-rich or P-rich by metalorganic vapor phase epitaxy (MOVPE). The preparation and surface reconstructions have been extensively studied experimentally as well as theoretically in the past.^{3,4} For InP, experiments showed that different atomic surface reconstructions significantly affect stability and the reaction path when in contact with water.⁵ However, the role of surface defects, indicated by Fermi level pinning, especially in contact with the liquid electrolyte, is still not fully understood, impeding further efficiency improvement of the photoelectrode. For that reason, the focus was redirected to the electrochemical interface of the semiconducting photoabsorber and the liquid electrolyte in the past decade.^{5–7} Furthermore, the interaction of InP as photoabsorber with water is also of high relevance when depositing conductive oxides as an electrochemical buffer layer using atomic layer deposition (ALD) where water frequently is used as oxide precursor.^{8,9}

We therefore investigated the P-rich InP (001) surface and its interaction with water using X-ray (XPS) and ultraviolet (UPS) photoemission spectroscopy as well as low-energy electron diffraction (LEED). In particular, we focus on the surface Fermi level position, which is found to be pinned close to midgap. *Ab initio* thermodynamics and band structure calculations show that this is related to surface defects. Furthermore, the surface reactivity of the defective surface in contact with water is investigated by modeling the semiconductor–electrolyte contact under ultrahigh vacuum (UHV) using the “frozen electrolyte” approach.¹⁰

2. EXPERIMENTAL DETAILS

Homoepitaxial InP (001) was grown on p-type InP (001) (Zn-doped, $(2\text{--}2.3) \times 10^{18} \text{ cm}^{-3}$ with 2° miscut toward the $\langle 111 \rangle$ direction) in a horizontal-flow MOVPE reactor (Aixtron, AIX-200) modified to

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enable a contamination-free transfer to UHV using H₂ as carrier gas. *tert*-Butylphosphine (TBP) and trimethylindium (TMIn) were used as precursors. Diethylzinc (DEZn) was used as a p-dopant source for the grown InP (001) epilayer. The molar flow of DEZn was adjusted to ensure a carrier concentration of $2 \times 10^{18} \text{ cm}^{-3}$ in the InP (001) epilayer, which was finally confirmed by electrochemical capacitance–voltage profiling. The growth was monitored by reflection anisotropy spectroscopy (RAS) which allows the specific preparation of the P-rich surface (see refs 11 and 12 for details). After sample preparation at TU Ilmenau, the sample was transferred via an UHV transfer shuttle with a base pressure of $\leq 5 \times 10^{-10}$ mbar¹³ to TU Darmstadt.

X-ray photoemission spectroscopy (XPS) measurements were conducted normal to the surface with a SPECS PHOIBOS 150 spectrometer using a monochromatic Al K α X-ray source (Focus 500 with XR50 M (SPECS) with $h\nu = 1486.74 \text{ eV}$) as part of the DAISY-FUN cluster tool. Survey and detail spectra were measured in fixed analyzer transmission mode with a pass energy of 20 eV (step size of 0.5 eV) and 10 eV (step size of 0.05 eV), respectively. The spectrometer was calibrated by yielding the Fermi level edge of Au, Ag, and Cu to 0 eV binding energy as well as Au 4f_{7/2} at 83.98 eV, Ag 3d_{5/2} at 368.26 eV, and Cu 2p_{3/2} at 932.67 eV binding energy with deviations $\leq 50 \text{ meV}$. Ultraviolet photoemission spectroscopy (UPS) measurements were conducted on the same spectrometer with pass energy of 5 eV (step size of 0.05 eV) using the HIS 13 Mono (Focus GmbH) as the monochromatic He II source with $h\nu = 40.81 \text{ eV}$ normal to the surface. Low-temperature water adsorption has been performed by cooling the manipulator with liquid nitrogen, leading to a substrate temperature of -176°C . Subsequently, the cooled manipulator was separated to another chamber with a base pressure of $< 10^{-9}$ mbar, and the sample was exposed to water using a leak valve. The dosage was controlled by the water pressure and the exposure time where a dose of 100 s at 10^{-8} mbar is defined as 1 langmuir (Lm).

3. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were performed using the Vienna Ab-Initio Simulation Package (VASP).¹⁴ The electron exchange and correlation effects were treated within the generalized gradient approximation (GGA) using the PBE functional.¹⁵ The electron–ion interaction was described by the projector-augmented wave (PAW) scheme.^{16,17} The surfaces were modeled using periodic supercells, consisting of a slab of thickness $\approx 18 \text{ \AA}$ for a total of 12 alternating In and P layers (six In and six P layers). The calculations were performed using a lattice parameter of $6.001 \text{ \AA}$, obtained from bulk calculations. A vacuum region of about $15 \text{ \AA}$ was used to decouple the material slab from its periodic image. The electric field in the vacuum region resulting from the two non-equivalent slab surfaces was quenched using a dipole correction. The wave functions were expanded into plane waves up to an energy cutoff of 500 eV. The surface Brillouin zone was sampled using a Γ -centered 4×4 k-point mesh. The first six layers were structurally relaxed until the forces acting on the atoms were below $0.02 \text{ eV/\AA}$, while the remaining six bottom layers were kept frozen in the bulk position. Allowing additional layers to relax produced no discernible effects. Band structure calculations for defect-containing 2×2 surface unit cells were performed within 4×4 translational symmetry, i.e., one defect per 4×4 supercell, to reduce spurious defect–defect interactions.

To determine the most favorable adsorption sites for water molecules and hydroxyl groups, potential energy surfaces (PES) were calculated using a mesh of 64 equidistant points. Here, the oxygen lateral degrees of freedom were constrained, while all other degrees of freedom were allowed to relax fully. Two and three different starting configurations were probed

for hydroxyl group and water molecule, respectively, at each mesh point.

The defect density N_i of some specific defect i was obtained from the Boltzmann distribution according to

$$\frac{N_i}{N} = \frac{e^{-\Delta G_i^f/k_B T}}{1 + \sum_{k \neq i} e^{-\Delta G_k^f/k_B T}} \quad (1)$$

where N is the total number of defect sites and T the temperature. The sum over k includes all defect models considered here. Assuming p-doped samples and energetically favorable neutral surface defects, the Gibbs free defect formation energy can be written as

$$\Delta G_f(p, T) = G_{\text{def}}(p, T) - G_{\text{ideal}}(p, T) - \sum_j \Delta n_j \mu_j(p, T) \quad (2)$$

Here G_{def} and G_{ideal} are the Gibbs free energies for surfaces with and without defects, respectively. They were calculated here including vibrational and electronic entropy¹⁸ as well as zero-point corrections in harmonic approximation. The last term in eq 2 accounts for the stoichiometry changes; i.e., Δn_j is the difference in the number of atoms of species j , and μ_j is the respective chemical potential. In the case of hydrogen desorption, the H chemical potential change $\Delta \mu_{\text{H}}$ with respect to an isolated molecule was calculated in the approximation of a two-atomic ideal gas in dependence on partial pressure p and temperature T following

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

where Z_{rot} and Z_{vib} are the rotational and vibrational partition functions, respectively, and λ is the de Broglie thermal wavelength of the H₂ molecule

$$\lambda = \sqrt{\frac{2\pi \hbar^2}{mk_B T}} \quad (4)$$

4. SURFACE CHARACTERIZATION AND FERMI LEVEL PINNING

The XP survey scan of the as-grown P-rich InP (001) surface reveals a very clean surface only showing emissions from In and P (Figure 1a). Especially, no traces of oxygen or carbon can be found at binding energy BE(O 1s) $\approx 530 \text{ eV}$ and BE(C 1s) $\approx 285 \text{ eV}$. The In 3d_{5/2} emission is located at 444.25 eV and can be fitted with a single Voigt line, indicating a homogeneous compound surface with no oxidized or segregated subspecies. The associated P 2p emission clearly contains a surface component which appears about 0.51 eV toward higher binding energies than the bulk-related emission at 128.45 eV with a relative intensity of $\approx 9\%$. We attribute this surface component to P dimers at the reconstructed surface.⁴ Surface core level shifts as measured in high-resolution synchrotron-induced photoelectron spectroscopy are not resolved due to their low binding energy shifts of $\leq 0.3 \text{ eV}$.¹⁹ Furthermore, the low-energy electron diffraction (LEED) patterns clearly reveal a 2×1 surface reconstruction, where the first-order spots are separated by diffuse streaks along the [110] direction (Figure 1b). The stabilization of buckled P dimers with atomic hydrogen, adsorbing during the MOVPE

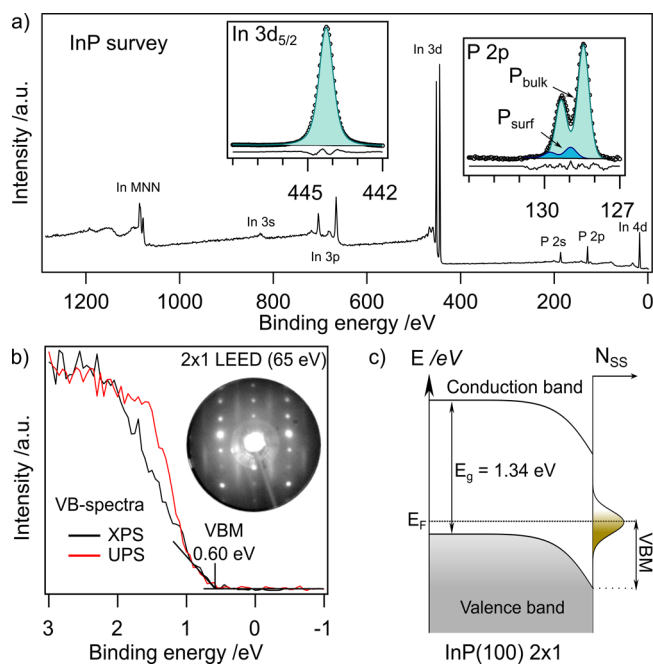


Figure 1. XP survey spectra of the prepared InP (001) surface with detail scans of In 3d_{5/2} and P 2p, including a surface component fit (a). XPS and UPS valence band cutoffs with surface LEED pattern at 65 eV (b). Scheme of surface band bending due to surface states distribution N_{SS} according to experimentally evaluated Fermi level E_F to valence band distances VBM depicted in (c).

process, because H_2 is used as carrier gas, can be arranged in-phase, resulting in a $p(2 \times 2)$ unit cell or out-of-phase corresponding to a $c(4 \times 2)$ unit cell.^{20,21} The superposition of both unit cells leads to the 2×1 -like LEED pattern with the characteristic streaks in the $\times 2$ half-order, indicating a 2×2 -2D-2H (two buckled P dimers with two atomic hydrogen) surface reconstruction at the present surface as predicted from *ab initio* calculations.³ For this very clean and homogeneous surface, the valence band maximum (VBM) is found to be at 0.60 eV, leading to a Fermi level position at the surface located slightly below midgap, when an InP band gap of 1.34 eV²² is considered. However, according to the doping concentration of the grown InP with zinc as a shallow acceptor of about $N_A = 2 \times 10^{-18} \text{ cm}^{-3}$, the Boltzmann term $k_B T$, and the effective valence band density of states N_{VB} of about $1.1 \times 10^{19} \text{ cm}^{-3}$,²² the Fermi level in the bulk is according to eq 5 expected to be $\approx 40 \text{ meV}$ above the VBM.

$$E_F - E_{VB} = k_B T \ln \left(\frac{N_A}{N_{VB}} \right) = 43 \text{ meV} \quad (5)$$

The discrepancy between measured and calculated Fermi level position relative to the valence band indicates a strong surface band bending of $V_{BB} = 0.56 \text{ eV}$ due to apparent surface states inducing electrons into the surface which pin the Fermi level as depicted in Figure 1c. Considering a parabolic potential drop inside the InP space charge region (SCR), the amount of total surface charges Q_{SS} can be calculated with eq 6, meaning that $<1\%$ of the surface atoms contribute to a charged defect.

$$-Q_{SS} = \sqrt{2\epsilon\epsilon_0 q V_{BB} N_A} = 3.9 \times 10^{12} / \text{cm}^2 \quad (6)$$

This raises the question, what surface defect originates from the initial surface band bending?

5. HYDROGEN-RELATED SURFACE DEFECTS

Atomic hydrogen from the MOVPE process is known to stabilize the InP (001) 2×2 -2D-2H surface, leading to completely filled and empty surface states close to the InP valence and conduction band edges, respectively, even though an occupied surface band is located slightly above the valence band.²³ For that reason, the observed Fermi level pinning at midgap has to result from surface defects inducing electronic states within the band gap of InP. Starting from the 2×2 -2D-2H surface, we consider four types of hydrogen-related defects, namely desorption and adsorption of one or two H atoms, respectively. The total probability of any of these defects can be calculated from eq 1, which is shown in dependence on temperature and partial H_2 pressure in Figure 2. At room

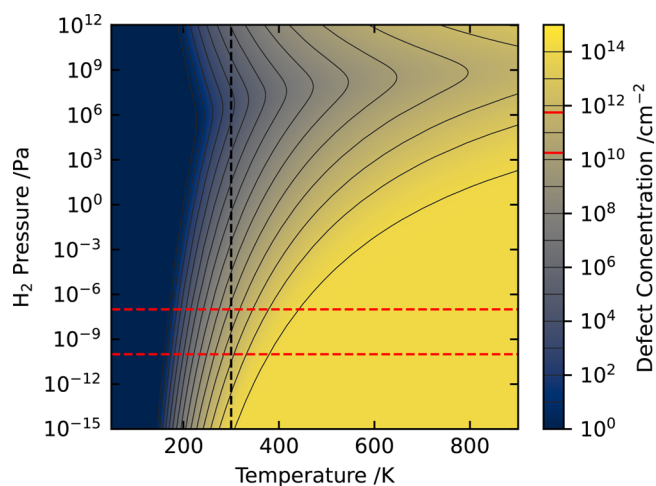


Figure 2. Hydrogen vacancy concentration on a InP (2×2)-2D-2H surface as a function of pressure and temperature. The black and red dashed lines depict room temperature and the ultrahigh vacuum range, respectively. The intersects of the dashed lines are depicted in the color bar by the red marks.

temperature and for typical UHV conditions with a hydrogen partial pressure in the range 10^{-10} – 10^{-7} Pa , a surface defect density on the order of 10^{10} – 10^{12} cm^{-2} can be expected. This is sufficient to lead to surface band bending but is slightly lower than the calculated surface charges experimentally evaluated from eq 6. However, the strong temperature dependency might also lead to a higher defect concentration because the prepared surface was transferred to UHV while cooling after the preparation procedure at 300°C . The desorption of one hydrogen atom from the 2D-2H surface is the by far predominant defect type under these conditions, leaving one phosphorus dangling bond at the surface. It corresponds to the formation of the InP (001) 2×2 -2D-1H surface. The other defects are very unlikely to be observed at the conditions modeled here. The adsorption of one additional H atom is the second most likely defect with a calculated density of $<10^{-3} \text{ cm}^{-2}$ and thus does not affect the surface band bending.

How do the surface electronic properties change upon H desorption? The band structure and the electron density of states (DOS) for the 2D-1H surface are shown in Figure 3. It reveals that the H vacancy gives rise to an in-gap surface state feature. The atom-resolved DOS demonstrates that this state is

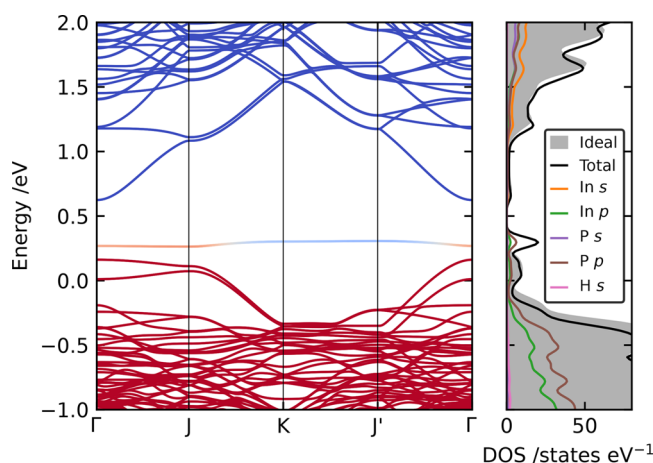


Figure 3. Band structure and atomic as well as orbital resolved electronic density of states of the InP (2×2)-2D-1H surface. The red/blue lines correspond to occupied/unoccupied bands. The energy of zero corresponds to the InP bulk valence band maximum. The shaded area represents the DOS for the ideal 2D-2H InP surface, without any defects.

of p character and is primarily due to the partially filled P dangling bonds. In comparison to the valence band spectra, the dangling bond feature is located slightly below the calculated midgap position, which is in good agreement to our photoemission spectra, indicating that the surface P dangling bond is the dominating defect causing the Fermi level pinning at the present P-rich InP (001) surface. Performing spin-polarized calculations does not change this picture: It leads to a splitting of the dangling bond state into an occupied spin-up state at the VBM and an unoccupied spin-down state in the band gap. The Fermi level will be pinned between these two states in the lower half of the band gap. The P dangling bond states of the intact 2D-2H surface are essentially not affected by the defect and occur close to the bulk VBM (see Figure 3 and ref 23).

6. WATER ADSORPTION

In a next step, the surface reactivity of the observed surface states upon water adsorption has been investigated experimentally. For that purpose, the sample–substrate was cooled with liquid nitrogen, and water from the gas phase was stepwise adsorbed by controlling water partial pressure and exposure time. As a final step, the cooling was stopped and the sample was measured at room temperature again.

After each step of exposure, XPS and UPS ($h\nu(\text{He II}) = 40.81 \text{ eV}$) measurements were conducted subsequently (Figure 4). The XP spectra clearly show a core level shift of In $3d_{5/2}$ and P $2p$ toward lower binding energies of about 0.27 eV after cooling the surface. This shift cannot be only explained by a freeze-out of acceptor states, shifting the Fermi level into the VBM at this temperature. The half-filled defect band leads to occupied states within the band gap and with that to a pinning of the Fermi level even at the ground state. Moreover, the cryogenic temperature enhances source-induced surface photovoltages because Shockley–Read–Hall recombination over surface states is reduced as described elsewhere.^{24–27} After the stepwise adsorption of water, both core levels reveal a shift toward higher binding energies and get damped by the growing water layer, rising the O $1s$ signal at $\approx 533 \text{ eV}$. As the shift shows a linear dependence on the water

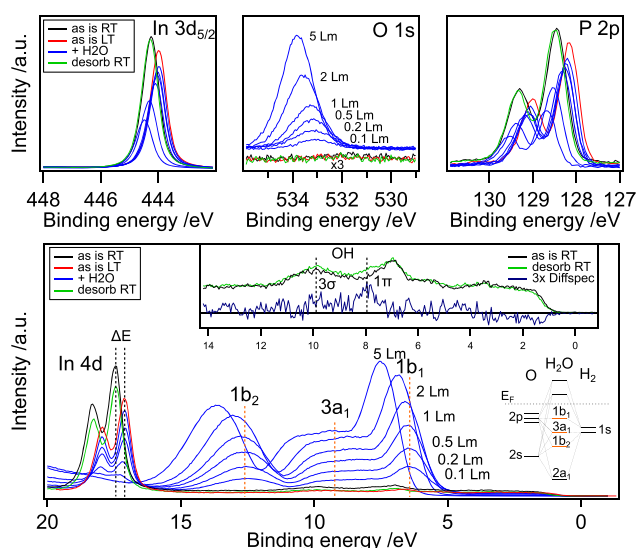


Figure 4. XP core level ($h\nu = 1486.74 \text{ eV}$, top) and monochromatic He II spectra ($h\nu = 40.81 \text{ eV}$, bottom) of low-temperature water adsorption on InP (001). The difference spectrum of the valence band before and after water adsorption as well as the LCAO approach of molecular water have been inset in UP spectra.

coverage even in the multilayer regime ($>1 \text{ Lm}$), we attribute it to a charging effect of the surface when the insulating ice layer charges due to the emission of photoelectrons. However, the water adsorption itself does not lead to any spectral changes in the core level lines, indicating a chemically immune surface upon water adsorption. After warming the surface back to room temperature, the water fully desorbs from the surface, and no O $1s$ emission remains to be observed. At the same time, the In and P core levels shift back to their initial energy positions, and no spectral changes are visible. With the He II UP spectra, a very surface sensitive In $4d$ emission spectrum can be measured (Figure 4, bottom). After cooling, the $4d$ core level shifts about $\Delta E = 0.33 \text{ eV}$ toward the Fermi level, similar as observed from the XP core levels. With higher water coverage, a characteristic water feature arises in the valence band with three features which can be attributed to the $1b_1$ (6.5 eV), $3a_1$ (8.5 eV), and $1b_2$ (12.5 eV) highest occupied molecular orbitals of molecular water.²⁸ The water features shift to higher binding energies with increasing coverage, indicating charging of the water layer similar as also observed by XPS. In contrast to the XP spectra, the In $4d$ line seems to be unaffected by the water layer. Only for coverages $>1 \text{ Lm}$ does the In $4d$ line slightly shift to higher binding energies, confirming that all core level shifts observed with XPS and UPS are source dependent and can be related to the charging of the topmost ice layer. For moderate charging of the ice layer, the InP core levels are not shifted as the substrate photoelectrons are equally retarded and accelerated when passing the charged layer. This apparently changes when the charging of the ice layer increases due to its increased thickness. In this case, also the substrate core levels reveal shifts to higher binding energies. Even though the photon flux of the monochromatized He II source ($\approx 10^{11} \text{ photons/s/mm}^2$) is in the range of the XPS source, the He II measurement is less susceptible to charging as the lower photon energy leads to less photoionization. After the desorption of the ice layers, the UP spectra reveal only slight spectral changes. However, at 8.0 and 9.9 eV, two features appear in the difference spectra, which

might be assigned to 1π and 3σ bonds of adsorbed OH groups,^{28,29} indicating a dissociation of adsorbed H_2O . Dissociative water adsorption has been reported for the InP (110)³⁰ as well as for the In-rich InP (001) surface.^{5,31} However, the weak signal in UPS and no signal in the XPS O 1s line indicate that OH is only present at a few surface sites far below a monolayer coverage. Furthermore, the LEED pattern still exhibits the 2×1 surface reconstruction, indicating that there are no structural changes after the desorption of water. As a conclusion from our experimental data, we state that, starting from a defective P-rich InP (001) surface, almost no electronic interaction with chemical bond formation to water is observed.

To verify our experimental findings, we determined the water adsorption configuration for the ideal 2×2 -2D-2H and the hydrogen-deficient surfaces computationally. The potential energy surface (PES) for single H_2O molecules adsorbed on the InP (001) 2×2 -2D-2H surface is shown in Figure 5 (left).

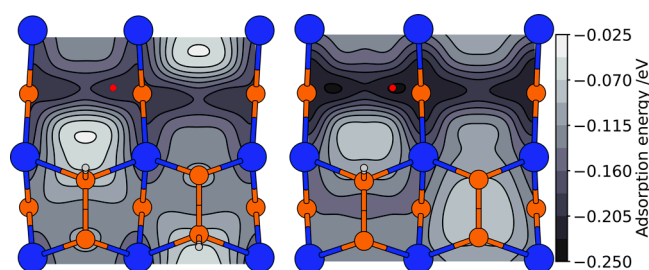


Figure 5. Calculated potential energy surfaces for single water molecules on InP (001) 2×2 -2D-2H (left) and 2×2 -2D-1H (right) surfaces. The red marks correspond to the most favorable adsorption sites. Blue and orange spheres indicate In and P, respectively.

Interestingly, the P dimer is not a favorable bonding site for water. This agrees with earlier findings for In-rich InP surfaces,^{31,32} where water adsorbs at In rather than on P sites. Here, the molecule preferably sits in the trench between the P dimer rows. In Figure 6, the equilibrium bonding geometry of a surface adsorbed water molecule is shown together with the calculated charge redistribution upon adsorption. There is a slight charge accumulation between the water proton and the P dimer up-atom, and a somewhat weaker charge accumulation between water oxygen and

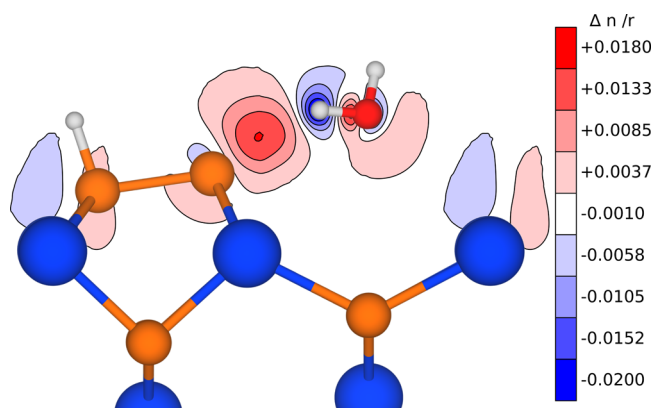


Figure 6. Structural configuration and water-induced charge redistribution for water adsorbed on 2D-2H. Red and blue isosurfaces indicate regions of charge accumulation and depletion, respectively.

second-layer In atom, leading to a weak physisorption. However, neither the atomic structure nor the electronic properties of the InP (001) 2×2 -2D-2H surface are strongly affected by the water adsorption. Calculated band structures (not shown here) reveal that water adsorption does not give rise to additional gap states.

Interestingly, the computational findings are very similar for the hydrogen-deficient, i.e., the InP (001) 2×2 -2D-1H, surface. However, compared to water adsorption on the 2×2 -2D-2H surface, a slightly larger (by about 0.03 eV) adsorption energy is calculated. The calculated PES indicates again adsorption preferentially in the trench between the P dimer rows (Figure 5, right). Here, the H_2O molecule bonds weakly to the P dimer, which is partially H saturated. For that reason, the electronic midgap state resulting from H desorption is not affected by water adsorption, confirming our experimental results, according to which no electronic nor chemical reactions could be identified upon the adsorption of molecular water.

The situation changes, however, as soon as water dissociation is considered. According to our experimental results, we could confirm slight traces of OH remaining after the desorption of molecular water. In Figure 7, the PES

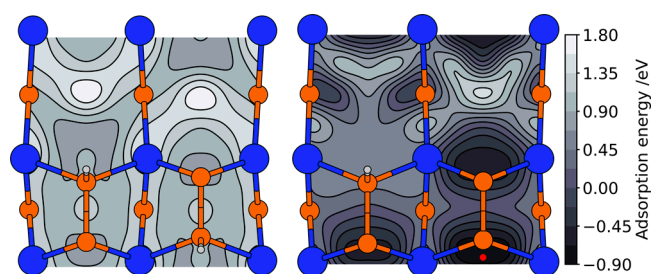


Figure 7. Calculated potential energy surfaces for hydroxyl group adsorption on InP (001) 2×2 -2D-2H (left) and 2×2 -2D-1H (right) surfaces. The red mark corresponds to the most favorable adsorption site.

calculated for OH adsorbed on InP (001) 2×2 -2D-2H (left) and 2×2 -2D-1H (right) is shown. Here the adsorption energy is calculated with respect to molecular water and is obtained as

$$E_{\text{ads}}(\text{OH}) = E_{\text{total}} - E_{\text{clean}} - E_{\text{OH}} \quad (7)$$

with

$$E_{\text{OH}} = E_{\text{H}_2\text{O}} - \frac{1}{2}E_{\text{H}_2} \quad (8)$$

The calculations shown in Figure 7 indicate that OH adsorption is favorable on the defective 2×2 -2D-1H surface, but not at all on 2×2 -2D-2H. With that the observed OH groups in the UP spectra could further indicate apparent P dangling bonds at the prepared InP (001) surface. In the case of the 2D-1H surface, the hydroxyl group adsorbs on the P dimer dangling bond, saturating the half-filled dangling P orbital resulting from H desorption. Accordingly, from calculated band structures (not shown here), the midgap surface state is removed, and the band structure resembles that of the surface without defects. It should be noted that the P dangling bond changes the adsorption energy not only at the dangling bond site itself but also on all P atoms of the 2×2 -2D-1H surface lattice.

Even though the UP spectra reveal adsorbed OH groups at the surface preferentially adsorbing on the H vacancy site, the Fermi level position within the band gap, and with that the surface band bending, remain unaffected after the adsorption of water, indicating that not all dangling bond defects could be passivated by the OH groups. This also confirms that the P dangling bond center itself is not the active site for water dissociation because beyond the H vacancy as a stable OH site, a neighboring active site for the remaining H adsorption as a further product of H₂O dissociation is missing. Furthermore, recent studies on In-rich InP (001) suggest that free In sites are required for the dissociation of molecular water on InP surfaces.³¹ For that reason, we suggest that water dissociation only occurs at step edges rather than on terraces of the P-rich InP (001) surface.

As a future perspective, additional experiments are planned exposing the P-rich InP (001) surface to acidic and basic aqueous solutions offering solvated H⁺ or OH[−] ions, which may strongly interact chemically to separated defect sites and may lead to a complete electronic surface passivation.

7. CONCLUSION

P-rich InP (001) was investigated by photoemission spectroscopy as well as DFT calculations. We found a strong surface band bending, which we attributed to hydrogen vacancies, leading to P dangling bonds and induce half-filled midgap surface states. Low-temperature water adsorption could not reveal a strong interaction of the molecular water with the present InP (001) surface. Our computational results could confirm that the considered dangling bond defect does not significantly change the adsorption behavior of the InP (001) surface compared to the hydrogen-saturated surface. After the desorption of molecular water, we could only find traces of remaining OH groups at the InP (001) surface, indicating a partial dissociation of the water molecule. Potential energy surface calculation reveals that, in contrast to H₂O, P dangling bonds strongly change the adsorption behavior of OH, which can passivate the midgap state after bonding to the dangling bond site. However, the remaining Fermi level pinning after water adsorption indicates that P dangling bonds are not the active sites for water dissociation on P-rich InP (001) surfaces as neighboring active sites for the dissociation of the H₂O molecule are missing.

AUTHOR INFORMATION

Corresponding Authors

Wolf Gero Schmidt – *Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany*; orcid.org/0000-0002-2717-5076; Email: W.G.Schmidt@upb.de

Wolfram Jaegermann – *Department of Materials- and Geosciences, Surface Science Laboratory, Technical University of Darmstadt, 64287 Darmstadt, Germany; Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany*; Email: Jaegermann@surface.tu-darmstadt.de

Authors

Dominik Christian Moritz – *Department of Materials- and Geosciences, Surface Science Laboratory, Technical University of Darmstadt, 64287 Darmstadt, Germany*; orcid.org/0000-0001-9859-3403

Isaac Azahel Ruiz Alvarado – *Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany*; orcid.org/0000-0002-4710-1170
Mohammad Amin Zare Pour – *Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany*
Agnieszka Paszuk – *Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany*
Tilo Frieß – *Department of Materials- and Geosciences, Surface Science Laboratory, Technical University of Darmstadt, 64287 Darmstadt, Germany*
Erich Runge – *Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany*; orcid.org/0000-0002-2157-229X
Jan P. Hofmann – *Department of Materials- and Geosciences, Surface Science Laboratory, Technical University of Darmstadt, 64287 Darmstadt, Germany*; orcid.org/0000-0002-5765-1096
Thomas Hannappel – *Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany*

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsami.2c13352>

Author Contributions

D.C.M. and I.A.R.A. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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