Angle Resolved Photoemission Spectroscopy
of the InP(001) surface

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Abstract

The P-rich (2 × 1)/(2 × 2) and the In-rich (2 × 4) reconstructions of InP(001) are studied by Angle Resolved Photoemission Spectroscopy (ARPES). Experimental results for the In-rich (2 × 4) InP(001) surface show two bound surface states and one surface resonance, located at −1.6 eV binding energy. This agrees well with ab-initio calculations. For the P-rich (2 × 1)/(2 × 2) InP(001) surface, neither theoretical nor experimental work regarding the electronic surface structure exists until now. We identify two possible surface states showing no discernible dispersion along the G±J and G±J directions of the surface Brillouin zone (SBZ). The energetically highest state, located close to the valence band maximum (VBM), is only observed along the [T10] direction and is most likely a P-dimer-bond state. The second state, located at −4.4 eV binding energy, is assigned to a surface resonance. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Despite their technological importance, atomic and electronic structure of the InP(001) surfaces have not been studied in great detail. Only recently, the atomic structure of the In-rich (2 × 4) InP(001) surface has been established [1], other reconstructions are not well understood yet [2–4]. Concerning the electronic surface structure of the In-rich (2 × 4) InP(001) surface, only few papers [5–9] have been published, and only one of these publications [8] presents a detailed

Angle Resolved Photoemission Spectroscopy (ARPES) analysis. For the even more important P-rich InP(001) surfaces, no work concerning the electronic structure exists to our knowledge. In this work, we present an ARPES study of the P-rich (2 × 1)/(2 × 2) and the In-rich (2 × 4) surface phases of InP(001). The atomic structure of the P-rich surfaces is addressed in Ref. [10].

2. Experimental details

Clean surfaces were prepared by Metal Organic Vapour Phase Epitaxy (MOVPE) growth of a Zn-doped buffer layer ($p = 10^{17}$ cm$^{-3}$) under P-rich
conditions on highly p-doped \((p = 10^{18} \text{ cm}^{-3})\) InP(001) substrates [11]. After growth, the samples were transferred from MOVPE conditions to ultra high vacuum [12], enabling sample transport in a mobile UHV vessel to the TGM2-beamline at the electron storage ring BESSY I in Berlin. ARPES data were taken with an ADES 400 electron spectrometer (angle resolution \(\leq 2^\circ\)) at different photon energies (20–30 eV) and along the \(\bar{\Gamma}-\bar{J}\) and \(\bar{\Gamma}-\bar{J}\) directions of the surface Brillouin zone (SBZ). The overall spectral resolution as determined by the Fermi edge of a polycrystalline Au sample in electrical contact with the samples was 150 meV at a photon energy of 25 eV. The measurement geometry of the photoemission experiments is shown schematically in Fig. 1. Binding energies are referred to the Fermi energy, if not stated otherwise. The Fermi energy is located at 0.7 eV above the valence band maximum (VBM), independent of the surface reconstruction. The chamber was equipped with a four grid reverse view Low Energy Electron Diffraction (LEED) optic and a strain free quartz window for Reflectance Anisotropy Spectroscopy (RAS) measurements. The RAS set-up is described in detail elsewhere [13]. Annealing of the samples was performed by thermal heating from the backside. Sample temperature was controlled by online optical measurements [14].

3. Results and discussion

Two different LEED patterns, corresponding to two different RAS line shapes, are reproducibly observed on the surfaces: a \((2 \times 1)/(2 \times 2)\) symmetry directly after transfer and upon annealing up to temperatures of 350°C [2,3,15], and a \((2 \times 4)\) symmetry upon annealing above 380°C [15]. The line shapes of the RAS spectra (discussed in Ref. [15]) are similar to the ones observed under growth conditions in MOVPE and Chemical Beam Epitaxy (CBE) [14]. They show characteristic features at spectral positions not related to bulk band gaps, as expected for surface transitions. Previous experimental and theoretical results consistently showed, that the

![Fig. 1. Upper panel: Schematic drawing of the photoemission geometry; the incident photon beam was fixed at an angle of 45° to the surface normal; the dispersion was measured by rotating the analyzer around the surface normal; angles are indicated in the plot. Lower panel: Schematic drawing of the \((1 \times 1)\) and \((2 \times 2)\) SBZ; high symmetry points are indicated. \(\bar{\Gamma}(1 \times 1)/\bar{\Gamma}(1 \times 1)\) correspond to the \(\Gamma_{11}/\Gamma_{10}\) points of the \((2 \times 2)\) SBZ.](image)
atomic structure of the In-rich (2 × 4) reconstruction is described by the so-called mixed-dimer model [1,9], where a P-In dimer along the [110] direction is formed on top of a complete In layer. In contrast, the atomic structure of the P-rich (2 × 1)/(2 × 2) reconstructed surface, recently observed by STM measurements [2–4], is not well understood yet. Two different atomic structures, exhibiting a similar LEED pattern, have been observed, depending on the P-coverage, i.e. growth conditions and/or annealing temperatures. The more P-rich one is believed to consist of P-dimers along the [110] direction, arranged in different, randomly distributed local arrangements on top of a complete layer of P. In our case, this surface is observed directly after sample transfer from the MOVPE growth [2,3].

Normal emission ARPES data at different photon energies recorded directly after sample transfer from the MOVPE growth chamber on the (2 × 1)/(2 × 2) reconstruction are shown in Fig. 2(a). Clearly visible are three structures (labeled S2, S3 and S4, indicated by arrows and dashed lines) not dispersing with photon energy. Additionally, a weak structure, slightly dispersing with photon energy, is seen at a binding energy of approximately −5.7 eV (labeled D5, also indicated by a dashed line). Clearly dispersing structures are indicated by solid lines. In Fig. 2(b), a calculated bulk band structure along the Γ−X symmetry line from Ref. [16] is shown, together with experimental peak positions. The \( k \) momentum of the photoelectrons was determined using the following relation between initial and final state energy \( E \):

\[
E_i = h\nu + \frac{\hbar^2}{2m^*}(k_{\perp \text{out}} + G) + V_0
\]

e.g. assuming a free electron parabola as final state and direct \( k \)-conserving transitions. Here \( m^* \) is the reduced electron mass and \( V_0 \) equals the inner potential. To fit the experimental data to the calculations,
a value of 7.7 eV for $V_\text{p}$ was used and for $m^*$, the free electron mass $m$ was taken. Only primary cone transitions (i.e. $G = (002)n_\perp$) were used. Compared to the relatively large range of values for the inner potential reported in literature for the InP(110) surface (i.e. 6 eV [18], referred to the VBM, and 9 eV [19]), this is a reasonable agreement with the value of 9 eV for a clean $(1 \times 1)$ InP(001) surface as reported in Ref. [6]. The two structures dispersing with $k_\perp$ are related to valence bands along the $\Gamma-X$ line of the bulk band structure (i.e. $\Gamma_6-X_5$ and $\Gamma_7-X_6$ in Ref. [16]). The three possible surface states not dispersing along $k_\perp$ are labeled S2, S3, and S4 and have binding energies of $-1$, $-1.8$ and $-4.4$ eV, respectively. Their dispersion with $k_\parallel$, taken at a photon energy of 28.4 eV is shown in Fig. 3(a). Due to the limited number of data sets (only few angles were probed), only the states S2, S4, and D5 (indicated by dashed lines) can be traced with certainty through the SBZ, whereas an assignment for state S3, apart from $\Gamma$, is impossible. In the valence band spectra of Fig. 3(a), recorded along the $[\overline{1}0\text{1}]$ direction, an additional weak shoulder (labeled S1 and indicated by a dashed line), located directly at the VBM, shows up. A better insight into the dispersion of these states can be gained from a surface band structure plot derived from the peak positions (Fig. 3(b)). They are plotted in the $(1 \times 1)$ SBZ on the projection of the bulk electronic states (shaded area, details of the calculation are given in Ref. [9]). State S1 and S4 fall into a gap of this projection on the $(1 \times 1)$ SBZ and show no discernible dispersion with $k_\parallel$, whereas D5, S3 and S2 overlap with the bulk band structure. The latter holds also for not labeled peaks, which are most likely bulk-related. Due to its broad line shape, the energetic position of D5 is too poorly defined to pinpoint its dispersion with $k_\parallel$. In the following, we will discuss therefore only the

![Fig. 3](image-url)

(a) Valence band spectra of the $(2 \times 1)/(2 \times 2)$ reconstruction along the $\Gamma-\overline{J}$ and $\Gamma-J$ symmetry lines of the SBZ, collected at a photon energy of 28.4 eV (indicated in the plot are emission angles and position in the $(1 \times 1)$ SBZ, for reference see Fig. 1); also indicated by arrows and/or dashed lines are S1, S2, S3, S4 and D5. (b) Surface band structure derived from experimental peak positions along the $\Gamma-\overline{J}$ and $\Gamma-J$ symmetry lines of the $(1 \times 1)$ SBZ; grey areas represent the projected bulk band structure; dashed lines present S1, S2 and S4. $\Delta E_{\text{VB}} = E_{\text{Fermi}} - E_{\text{VBM}}$. 


states S1, S2, and S4 in more detail. S2 shows a clear dispersion symmetric to the $\bar{J}$ and $\bar{J}'$ points of the $(1 \times 1)$ SBZ, in contrast to a dispersion symmetric to the $(2 \times 2)$ SBZ, as expected for a surface state. Its largest intensity is observed around the $\bar{J}$ and $\bar{J}'$ points of the $(1 \times 1)$ SBZ. This behaviour would be expected for an umklapp process with $g_\parallel = (001)_{\parallel}$ [20], which is very likely because of the poor long range order of the surface. We assign S2 therefore to an umklapp process related to the highest bulk valence band along the $\Gamma - L$ direction [16]. S4 clearly shows all necessary characteristics for a bound surface state/resonance: it does not disperse with the photon energy nor with $k_\parallel$ and falls partially into a gap of the bulk band structure. Furthermore, no particular bulk bands to which it could be related either by umklapp processes or joint density of states effects are energetically close. Additionally, it is reconstruction dependent and disappears completely on the $(2 \times 4)$ reconstructed surface (see Fig. 4). A possible explanation for the non-observable dispersion of S4 is again either the limited number of data points or a very weak interaction with the corresponding states in neighbouring surface unit cells. The latter explanation was already used in Ref. [8] for the non-observable dispersion of a surface state on the $(2 \times 4)$ InP(001) surface. Another very simple explanation would be a broadening of valence band structures because of the mentioned poor long-range order [2,3]. We assign the state S4 therefore to a surface state which is in resonance with the bulk over large parts of the SBZ. S1 shows exactly the characteristics one would expect for a symmetric dimer-bond related surface state: it is close to the bulk VBM and only observed for a $k_\parallel$ component along the $[110]$ direction. This indicates a vanishing dipole matrix element for a wave function symmetric in the surface plane. If this state were related to a

![Figure 4](image_url)

**Fig. 4.** (a) Valence band spectra of the $(2 \times 4)$ reconstruction along the $\Gamma - J$ and $\Gamma - J'$ symmetry lines of the SBZ, collected at a photon energy of 21.4 eV (indicated in the plot are emission angles and position in the $(1 \times 1)$ SBZ, for reference see Fig. 1); also indicated by arrows and/or dashed lines are S1*", S1*'*, and S2. (b) Surface band structure derived from the experimental peak positions along the $\Gamma - J$ and $\Gamma - J'$ symmetry lines of the $(1 \times 1)$ SBZ; grey areas represent the projected bulk band structure; dashed lines present S1", S1*'*, and S2. $\Delta E_{\text{VB}} = E_{\text{Fermi}} - E_{\text{VBM}}$. 


surface- or bulk-umklapp process, one would firstly expect to find symmetric emission properties and secondly, its intensity to be different at the \( J(2 \times 2) \) and \( J(1 \times 1) \) points, which is not observed. We therefore relate it to a P-dimer bond state.

The valence bands taken on the In-rich \((2 \times 4)\) reconstruction (Fig. 4(a)) with a photon energy of 21.4 eV show a completely different line shape, indicating a different electronic structure of the surface. The surface band structure derived from experimental peak positions is shown in Fig. 4(b). The In-rich \((2 \times 4)\) reconstructed surface was already shown in Ref. [8] to exhibit two surface states, \( S_1 \) and \( S_2 \), at binding energies of \(-1.0 \) and \(-1.8 \) eV \((-1.6 \) eV in our study\) at the \( \Gamma \) point. In Ref. [8], the non-discernible dispersion of these states was explained by a weak electronic interaction between neighbouring surface unit cells. Our data are taken with a better spectral resolution, and show that the highest level state, labeled \( S_1 \) in Ref. [8], consists of two distinct contributions, labeled \( S_1^- \) and \( S_1^+ \) in the plots, whereas for \( S_2 \), the experimental results of Ref. [8] are nearly confirmed. To determine the origin of these states, we performed density-functional-theory calculations (details similar to Ref. [9]) on the mixed-dimer model of the \((2 \times 4)\) \( \text{InP}(001) \). From these calculations, we assign \( S_1^- \) to \( \sigma \)-like bonds between the uppermost In atom and the two surface cations below. \( S_1^+ \) corresponds to the dangling \( p \)-orbital at the P dimer atom. \( S_2 \) is most likely related to the \( \sigma \)-bond of the mixed dimer, formed by in-plane \( \text{In} \) \( sp^2 \)-hybrids and \( P \) \( p \)-orbitals. About 0.5–1 eV lower in energy are the \( \sigma \)-bonds between the uppermost \( P \) atom and the second-layer surface cations. These bonds are tentatively assigned to the measured surface state energies around \(-1.5 \) eV (referred to the VBM). A more detailed discussion of these bands for the very similar case of the Ga-rich \((2 \times 4)\) \( \text{GaP}(001) \) is given in Ref. [21].

4. Conclusions

We studied the electronic surface structure of the P-rich \((2 \times 1)/(2 \times 2)\) and the In-rich \((2 \times 4)\) \( \text{InP}(001) \) surface with ARPES. Two surface states are identified for the \((2 \times 1)/(2 \times 2)\) surface, at \(-0.7 \) and \(-4.4 \) eV binding energies, respectively. We associate the highest level state with a P-dimer bond, whereas the second state is assigned to a surface resonance. On the \((2 \times 4)\) reconstructed surface, two bound surface states, located partially above the bulk band projection and one surface resonance at \(-1.6 \) eV, are identified, in agreement with ab-initio calculations of the electronic surface structure for the mixed-dimer model of the \((2 \times 4)\) surface.

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