

# Core and valence-level photoemission study of the InP(001)-(2×1)S surface: Surface structure and electronic states

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(Received 20 October 1999)

The *ex situ* sulfur treatment of InP(001) by  $(\text{NH}_4)_2\text{S}$  and subsequent annealing *in situ* finally results in a sulfur-induced  $(2\times 1)$  superstructure as observed by low-energy electron diffraction. We have investigated the development of the In  $4d$ , P  $2p$ , and S  $2p$  core levels with increasing temperature by using soft x-ray photoelectron spectroscopy. The measured core level shifts are compared with the corresponding data obtained on the  $(2\times 4)$  reconstruction of the clean InP(001) surface. On the basis of the core level data some models of the  $(2\times 1)$ S structure are discussed. Valence-band photoelectron spectra of the  $(2\times 1)$ S and the  $(2\times 4)$  surfaces have been measured in dependence on photon energy at normal emission and derived  $E(k_\perp)$  dispersions are analyzed. Although significantly different surface features are observed on both surfaces, there are similarities, which may be interpreted in terms of contributions from similar structural elements, possibly surface dimers.

## I. INTRODUCTION

Sulfur treated III-V(001) surfaces have received much attention during the last years because of the achieved improvement of chemical and electronic surface and interface properties. Improved stability against oxidation at ambient conditions and greatly enhanced photoluminescence (PL) intensities were reported for ammonium sulfide  $(\text{NH}_4)_2\text{S}$  treated surfaces.<sup>1</sup> High PL intensities at  $\text{SiN}_x/(\text{NH}_4)_2\text{S}/\text{InP}(001)$  insulator-semiconductor interfaces and increased lifetimes of metal-insulator-semiconductor (MIS) devices were attributed to sulfur-induced electronic and chemical passivation, and these observations were related to reduction of the density of gap states.<sup>2</sup>

The *ex situ*  $(\text{NH}_4)_2\text{S}$  treatment of InP(001) typically results in  $(1\times 1)$  low-energy electron diffraction (LEED) pattern, which transforms into a  $(2\times 1)$  after annealing in UHV. These sulfur-induced structures have been investigated intensively using photoemission techniques as XPS,<sup>3-8</sup> diffraction techniques (XPD),<sup>4-6</sup> scanning tunnelling microscopy (STM),<sup>9</sup> and theoretical simulations of the structural and electronic properties.<sup>8,11</sup> Experimental determinations of the band structure have so far focused on angle-resolved ultraviolet photoemission spectroscopy (ARUPS).<sup>12</sup> Only one investigation relating photoemission along  $\Gamma-X$  on InP is known.<sup>13</sup> Nevertheless, there is still large scatter in the reported data regarding the obtained number of sulfur species, their assignment, and the structural ideas, which may possibly be related to differences in the preparation procedures to a great extent.

In this paper we present surface-sensitive core level spectra as well as energy-dependent valence-band measurements of the  $(2\times 1)$ S, prepared by *ex situ* sulfurization and annealing. The derived  $E(k_\perp)$  dispersions are analyzed in order to

separate bulk states from nondispersing states, which are candidates for surface-related features. Both core and valence-band data are compared to corresponding measurements on the  $(2\times 4)$ , and from this analysis a consistent structural models is proposed for the  $(2\times 1)$ S at low sulfur coverages.

## II. EXPERIMENT

The experiments were performed at the beamline TGM 3 (BESSY I) using an angular-resolving VG ADES 400 spectrometer. The overall resolution was 200 meV at  $h\nu = 25$  eV, 280 meV at 60 eV. Core-level spectra were taken in normal emission at 60 eV (In  $4d$  and VB) and 190 eV (S  $2p$ , P  $2p$ , and In  $4d$ ). Valence-band spectra were recorded for photon energies  $h\nu = 15-30$  eV in steps of 0.5 eV in normal emission, too. The preparation of the *n*-type InP(001) samples ( $2\times 10^{18}$  cm<sup>-3</sup>, supplied by CrysTec) was performed under nitrogen atmosphere using a glove bag. The samples were etched in fluoric acid, dipped in methanol, and immediately immersed in ammonium sulfide  $(\text{NH}_4)_2\text{S}$ . Finally, the samples were rinsed in methanol, blown dry with nitrogen, and transferred into UHV. Annealing to 300 °C significantly improved the weak  $(1\times 1)$  LEED pattern of the *ex situ* prepared samples. The  $(2\times 1)$ S superstructure was obtained at 350–360 °C. The remaining sulfur coverage was estimated to be only slightly in excess of 0.5 monolayers (ML's) for this surface. The  $(2\times 4)$  reconstruction (with twofold spots along  $[1\bar{1}0]$ ) investigated here was prepared by sputter ( $\text{Ne}^+$ ) and annealing (380 °C) cycles as described elsewhere.<sup>14</sup> Note that further annealing  $\geq 400$  °C of the sulfur-induced  $(2\times 1)$  also changes the LEED pattern to  $(2\times 4)$ , but this is accompanied by metallic features in the photoelectron spectra including a Fermi edge in the valence

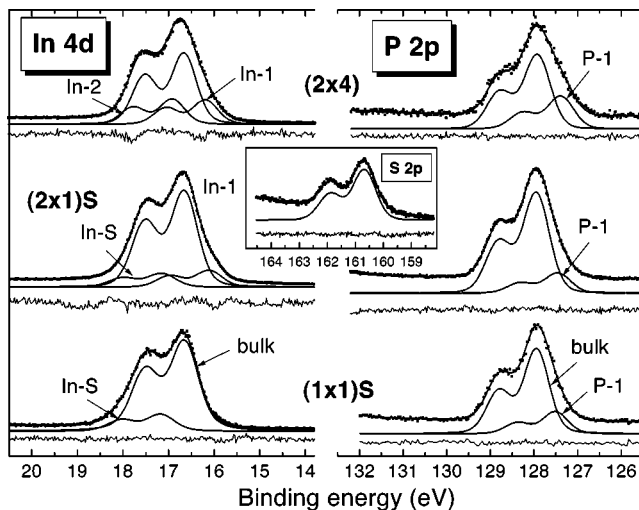


FIG. 1. The In  $4d$  (left) and P  $2p$  (right) photoelectron spectra of the  $(1 \times 1)S$  (bottom), the  $(2 \times 1)S$  (center), and the  $(2 \times 4)$  (top) reconstructed InP(001) surface. The used photon energy was 60 eV for In  $4d$ , 190 eV for P  $2p$  and S  $2p$ . Inset: the S  $2p$  line of the  $(2 \times 1)S$ .

band, indicating surface damage. All binding energies (BE) are referred to the valence-band maximum (VBM), by following the In  $4d$  core level and applying  $E(\text{In } 4d_{5/2} \text{ bulk}) - E(\text{VBM}) = 16.65 \text{ eV}$ .<sup>15</sup> The numerical decomposition of the core-level spectra is described in detail elsewhere.<sup>14,16</sup>

### III. RESULTS AND DISCUSSION

The core-level spectra of the sulfur-treated InP(001) surface at different stages of preparation recorded at surface-sensitive conditions are presented in Fig. 1 in comparison with the corresponding spectra of the clean  $(2 \times 4)$ -reconstructed surface. A cursory inspection by eye reveals only minor indications for additional components in the peaks but the fit procedure permits a reliable analysis, as may be indirectly concluded from the residuals shown below spectra and fit components. All P  $2p$  spectra displayed on the right-hand side of Fig. 1 require the inclusion of a surface component P-1 at slightly lower BE compared to the dominating bulk P  $2p$  doublet. The determined surface core-level shifts (SCLS) are quite close and correspond to SCLS =  $-0.47$ ,  $-0.48$ , and  $-0.45 \text{ eV}$  in the case of the  $(2 \times 4)$  (top),  $(2 \times 1)S$  (center), and  $(1 \times 1)S$  (bottom), respectively. P-1 may be associated to lower-coordinated phosphorus in the surface. In contrast, the numerical analysis of the In  $4d$  spectra, shown on the left-hand side of Fig. 1, had to include up to two surface-related components in addition to the bulk contribution. Surface components at lower BE, exhibiting SCLS =  $-0.45$  and  $-0.52 \text{ eV}$ , are only detected for In  $4d$  spectra of the clean  $(2 \times 4)$  (top) and the  $(2 \times 1)S$ , respectively. The annealing-induced appearance of this In-1 component in addition to the single component S  $2p$  spectrum (see Fig. 1, center) is a striking spectroscopic feature, which accompanies transformation of the LEED pattern on the sulfur-treated InP(001) surface to a  $(2 \times 1)S$ . Surface components at higher BE (In-2 or In-S) are observed for all In  $4d$  spectra at SCLS values of  $+0.30$ ,  $+0.53$ , and  $+0.52 \text{ eV}$ , in the case of the  $(2 \times 4)$  (top),  $(2 \times 1)S$  (center), and

$(1 \times 1)S$  (bottom), respectively. The results are in very good agreement with the existing core level studies on the  $(2 \times 4)$  (Refs. 18, 24, and 25) and the  $(1 \times 1)S$ .<sup>1,3,4</sup>

The high BE In  $4d$  component (In-S) observed on the sulfurized surface were attributed to In-S bonds, previously.<sup>1,3,4</sup> An interpretation of the surface components observed on the clean  $(2 \times 4)$  was recently related to the mixed In-P dimer reconstruction, which represents the lowest energy surface structure of the cation-rich InP(001) as suggested by Schmidt *et al.*<sup>17,18</sup> In this manner the In  $4d$  component In-2 at the higher BE was assigned to threefold coordinated In atoms at the clean surface. The surface component In-1 at lower BE was assigned to fourfold coordinated surface In atoms, which are characterized by an In-rich environment due to In-In bonds. The surface component P-1 of the  $(2 \times 4)$  was attributed to lower-coordinated surface phosphorus as mentioned above, most likely P in the mixed dimer.

In order to provide a base for the interpretation of the surface core-level spectra of the  $(2 \times 1)S$  we propose a simple structural model, which fulfills the electron counting rule.<sup>10</sup> The substrate core levels of the  $(2 \times 1)S$  and the  $(2 \times 4)$  are strikingly similar with respect to the number of surface (or shifted) components, the sign of the shifts and even the magnitude of the core-level shifts. This similarity of the core-level spectra is a first hint for a similar surface structure. Therefore the model includes the most prominent structural element of the  $(2 \times 4)$ , the mixed dimer. Guided by the single component S  $2p$  spectrum of the  $(2 \times 1)S$  (Fig. 1, center) and the low S coverage we restrict ourselves to those models which possess just one S component, which we tentatively place on a substitutional site ( $S_p$ ) in the first subsurface P layer. This is in accordance with results of several groups.<sup>4-7</sup> On top of the In surface layer a mixed In-P dimer is formed. However, this base model for a sulfur-induced  $(2 \times 1)$  dimer-based superstructure may be easily modified to derive related models, which also fulfill electron counting. An exchange of In atoms by P or vice versa in the dimer or an exchange of the S in the P layer with P from the dimer or a shift of the S in the second layer will not violate electron counting. In this manner mixed In-S dimers, In-In cation dimers, P-P anion dimers, or mixed P-S dimers may be generated from the initial mixed In-P dimer model by suitable atom exchange. Specific examples for such models are displayed in Fig. 2.

The mixed In-P dimer model of Fig. 2(a) permits us to reasonably explain the surface components on the  $(2 \times 1)S$  in analogy with the interpretations given in case of the  $(2 \times 4)$ , keeping in mind a likely energetic overlap of threefold coordinated In and In-S contributions. Problems in the interpretation arise for assignment of the surface components in case of the other models. Evidently, the P-1 surface component is difficult to explain in case of the In-In cation dimer [Fig. 2(b)] and the mixed In-S dimer model. Further, obvious interpretation for In-1 is lacking in case of the P-P anion dimer [Fig. 2(c)] and the mixed P-S [Fig. 2(e)]. In summary, the proposed mixed In-P dimer model involving incorporated sulfur on P sites offers the most straightforward interpretation of the surface components on  $(2 \times 1)S$  among the structural models considered above.

The valence-band structure of the InP(001)- $(2 \times 1)S$  and

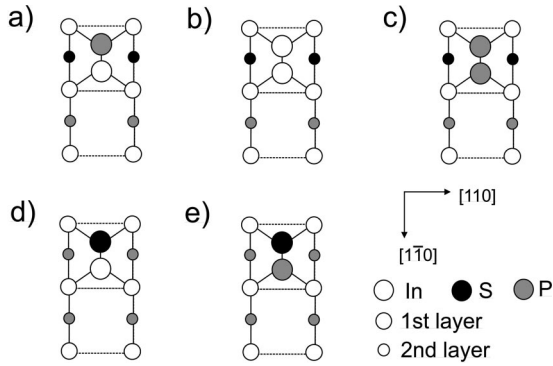


FIG. 2. Some possible models of the  $(2 \times 1)S$ : (a) a mixed In-P dimer on top with a filled dangling bond at the anion, sulfur built in on P site below the dimer; (b) a cation In-In dimer; (c) an anion P-P dimer; (d) a mixed In-S dimer on top, no S built in; (e) a mixed P-S dimer, no S built in. The white circles mark In, gray mark P, the black circle is S, the atoms on top are bigger than the atoms in the layers below.

the  $\text{InP}(001)-(2 \times 4)$  was studied by following the evolution of the states with photon energy at normal emission, i.e., at  $\bar{\Gamma}$  in the surface Brillouin zone (SBZ). The derived  $E(k_{\perp})$  dispersion allows us to distinguish between dispersing bulk-related features and nondispersing states, which may be due to surface-related states (surface states, surface resonances) and adsorbate-induced states or due to indirect emission from density-of-states features. A set of experimental valence-band spectra obtained on  $(2 \times 1)S$  is plotted in Fig. 3. Inspection by eye already reveals the existence of dispersing states as well as nondispersive features. At photon energies below 18 eV the In  $4d$  peak excited by second-order light crosses the upper valence-band region and complicates the analysis. Analogous sets of spectra were also recorded for the  $(2 \times 4)$  (not shown).

The experimentally derived dispersions  $E(k_{\perp})$  are presented in Fig. 4 for both  $(2 \times 1)S$  and  $(2 \times 4)$ . Inner potentials  $V_0 = -7.5$  and  $7.7$  eV were used for the determination of  $k_{\perp}$  data<sup>19</sup> in Fig. 4 on  $(2 \times 1)S$  and  $(2 \times 4)$ , respectively. These values are close to  $V_0$  values of  $-9$  eV (Refs. 13 and 20) and of  $-7.7$  eV (Ref. 21) applied for the analysis of  $E(k_{\perp})$  dispersions from other surface orientations or reconstructions on InP, keeping in mind that the surface structure will also influence  $V_0$  to some extent.<sup>19</sup> We emphasize the very good accordance of the dispersing states V1 and V2 of  $(2 \times 1)S$  and  $(2 \times 4)$ , and the good matching of these experimental states with the solid lines provided in Fig. 4, which represent the dispersion of two bulk bands along  $\Gamma-X$  as calculated by Chelikowsky and Cohen<sup>22</sup> and presented in Refs. 13 and 21.

Unfortunately, the accessible photon energies of 15–30 eV were not sufficient to cover the whole  $\Gamma-X$  line and a comparison to available experimental bulk state energies at  $\Gamma$  and  $X$  is not possible. We can find several nondispersing structures in Fig. 4 denoted by S1, S2 (low BE), and A–D (higher BE). The peak D at  $5.9 \pm 0.1$  eV is clearly due to the well-known density-of-states (DOS) feature reported frequently<sup>13,20,23</sup> (from the  $X_6$  point of the BZ). The feature B at  $3.5 \pm 0.1$  eV was attributed to the bulk emission from the  $\Sigma_{1,min}$  point.<sup>13,22,23</sup> In contrast to these DOS-derived

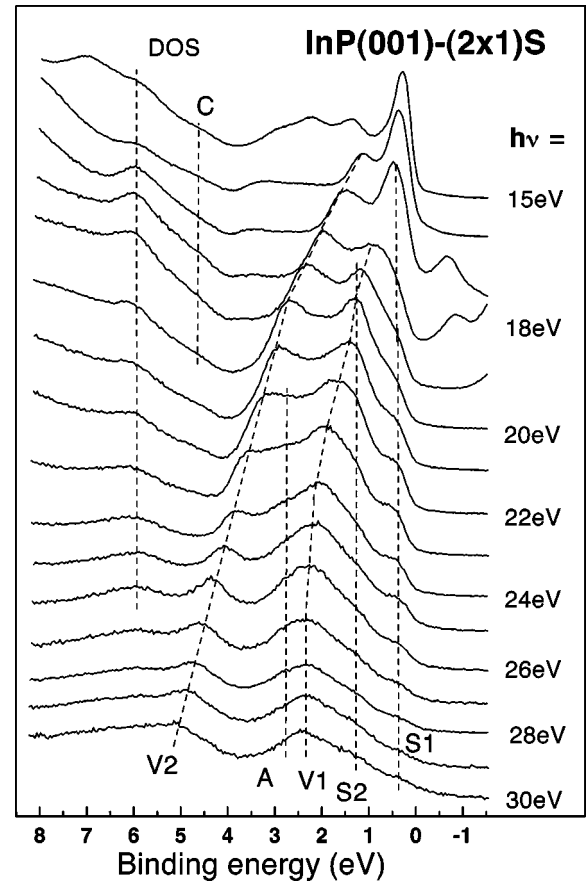


FIG. 3. Valence-band spectra of the  $(2 \times 1)S$  surface recorded with  $h\nu = 15\text{--}30$  eV in normal emission.

peaks B and D, which may be found on both  $(2 \times 1)S$  and  $(2 \times 4)$ , features A and C are detected on the  $(2 \times 1)S$  only. Further investigations are needed to identify the origin of these features.

The topmost nondispersive feature S1 at  $0.3 \pm 0.1$  eV on the  $(2 \times 1)S$  can be observed throughout the whole range of spectra along the  $\Gamma-X$  line of the BZ. This peak can be directly related to the surface-derived state found in the ARUPS studies by Mitchell *et al.*<sup>12</sup> Its energy position is

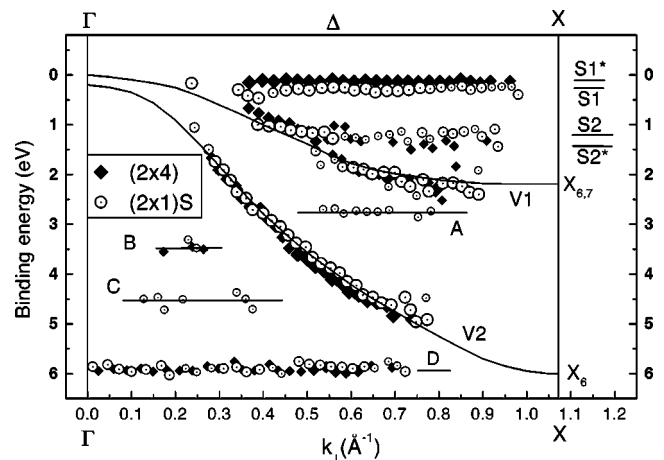


FIG. 4. Experimental dispersions  $E(k_{\perp})$  for the  $(2 \times 1)S$  (open circles) and the  $(2 \times 4)$  (filled diamonds) surfaces along  $\Gamma-X$ ; the solid lines are calculated bands from Refs. 13 and 22.

slightly but reproducibly below the  $S1^*$  state at  $0.1 \pm 0.1$  eV observed on  $(2 \times 4)$ , which can be clearly assigned to the well-known surface state on this surface.<sup>24,25</sup> The feature denoted  $S2$  is much weaker in intensity than  $S1$ . It seems to degenerate with the states of the bulk bands  $V1$  and  $V2$  at photon energies closely corresponding to He I and Ne I, respectively. This might be an explanation for the fact that no similar feature was reported in the ARUPS study by Mitchell *et al.*<sup>12</sup> On the  $(2 \times 4)$  a nondispersing feature  $S2^*$  is observed at similar energy  $-1.4 \pm 0.2$  eV. On this surface similar structures near 1 eV BE were also found in Refs. 21 and 26, and they were also assigned to surface-related states.<sup>26</sup> Note that on our  $(2 \times 1)S$  no surface states are observed in the fundamental gap at  $\Gamma$ , which were predicted for the case of a sulfur-rich  $(2 \times 1)S$  by Ferraz and Srivastava.<sup>11</sup> Evidently, our route of preparation lead to a loss of sulfur, and thus the investigated surface does not adopt this predicted structure.

This comparison of the states at the two surfaces has shown that surface-related electronic states on the  $(2 \times 1)S$  and the  $(2 \times 4)$  are somehow similar but slightly different in

energy. Schmidt *et al.*<sup>17</sup> calculated the surface electronic states of the mixed dimer  $(2 \times 4)$ . At  $\bar{K}$  in the SBZ he found several surface states, which could be related to the occupied P dangling bond and the bonds of the mixed dimer, including also In-In bonds. Probably, the surface-related peaks observed in our energy-dependent study of the  $(2 \times 4)$  can be traced back to the dimer, too. Summarizing briefly, in the light of the previous discussion of the surface core levels in a fingerprinting way, now we may suggest also from the valence-band structure that structural similarities occur for the  $(2 \times 1)S$  and the  $(2 \times 4)$ . Hopefully, this proposal can stimulate further theoretical work in order to solve this question.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the support by the groups of K. Horn and H. Kühlenbeck (FHI Berlin) at BESSY I. Financial support was supplied by BMBF (Grant No. 05 SE8 OLA 7).

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