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Sulfur passivated InP(100): surface gaps and electron counting

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Abstract

The atomic and electronic structures of the sulfur passivated InP(100) surface have been studied with electron diffraction, photoemission and inverse photoemission spectroscopies. The InP(100) surfaces were passivated using a wet chemical treatment. In agreement with previous studies, we find that the unannealed surface has the 1×1 symmetry of the bulk lattice, which transforms to a 2×1 pattern upon annealing to temperatures in the range 350–500°C. Photoemission and inverse photoemission studies of the electronic states in the vicinity of the valence band maximum and conduction band minimum demonstrate that the passivation process removes states from the region of the fundamental gap of InP. No bands cross the Fermi level. The dispersion of several two-dimensional states has been measured. These states show a strong similarity to surface states of the Ge(100)-S(1 ML)(1×1) system. By applying electron counting rules, we demonstrate that several of the surface structural models that have been proposed to date are inconsistent with our experimental results, since they should result in partially filled surface bands crossing the Fermi level.

1. Introduction

Within the last few years attempts have been made to formulate a small number of physical principles that have general utility in identifying equilibrium semiconductor surface structures [1,2]. This field has recently been reviewed by Duke [3]. Considerable progress has been made and this is due, in part, to the fact that many semiconductor surface structures have been solved [4]. The motivation has been to look beyond individual surface structures to find the common principles that govern their formation. Although it is clear that the main driving force for semiconductor surface reconstruction is the formation of surface bonds that saturate the valence of the surface atoms, other factors are also important. For example, because the surface atoms terminate a three dimensional lattice the bonding constraints are quite different from the constraints imposed by either bulk or small molecule coordination. Surface relaxation often places the substrate under elastic stress and consequently the surface layer may be considered to be epitaxially constrained.

In this paper we have examined the atomic and electronic structure of the S-passivated InP(100) surface. The passivation process is interesting in itself because it reduces the density of gap states on the InP(100) surface and consequently this allows a greater degree of Fermi level movement [5]. As would be expected, the reduction in the density of gap states also improves the quality of Schottky contacts to InP [6], and the Schottky barrier height extracted from diodes fabricated on the S-passivated

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surface exhibits a stronger dependence upon the work function of the metal overlayer [7]. In this paper we will discuss the atomic and electronic structure of the monolayer system. From a fundamental point of view the system is sufficiently simple to allow us to apply the general principles described above, and demonstrate that several of the structural models that have been proposed for this system are inconsistent with our experimental finding that there are no partially filled electronic bands at the Fermi energy.

2. Experimental

The experiments were performed in an ultra high vacuum (UHV) chamber which has a base pressure of 8×10^{-11} Torr. All photoemission and inverse photoemission measurements are angle-resolved. The photoemission experiments were performed with a differentially pumped resonance lamp and a hemispherical electron energy analyzer with a 50 mm mean radius. The inverse photoemission experiments were performed with a home-built electron gun [8] and a bandpass photon detector consisting of a CaF_2 window and a Cu–Be electron multiplier [9,10]. The photoemission and inverse photoemission energy scales can be aligned by using the hemispherical analyzer to measure the kinetic energy of electrons produced by the electron gun [11]. This allows us to accurately measure gaps between occupied and unoccupied states without resorting to a secondary reference. The low-energy electron diffraction (LEED) studies were performed using a Princeton Research Instruments RVL 8-120 reverse view LEED system. The samples were mounted on Mo sample holders and transferred from atmosphere into UHV through a custom load lock system which is evacuated using a turbomolecular pump.

Epiready n-type InP(100) wafers (Crystacomm), both unintentionally doped with a carrier density of 5.6×10^{15} cm^{-3} and Sn doped with a carrier density of 1.2×10^{18} cm^{-3}, were used in the experiments. The wafers were immersed in ammonium sulfide solution (20.1% $(NH_4)_2S$) for 15 min at a temperature of 65°C. They were then dipped in ammonium sulfide solution (20.1% $(NH_4)_2S$) at room temperature and blown dry with Ar. Sample mounting was also performed while blowing Ar over the sample. The samples were transferred directly into UHV and annealed at 350°C in order to remove physisorbed gases and to order the overlayers. The principal gases found to be desorbing from the samples were H_2O, SO_2, and NH_3. The samples were brought up to the annealing temperature slowly and left at that temperature for 5–10 min. The photoemission results were found to be reproducible after multiple annealing cycles. No differences were observed in the results for the unintentionally n doped and Sn doped samples.

The photoemission results reported here were obtained after annealing at 350°C as described above. LEED studies were performed as a function of annealing temperature. In each case the sample was annealed at the specified temperature for approximately ten minutes. The sample was allowed to cool to room temperature before taking the LEED data.

Photoemission and inverse photoemission studies were also performed on clean InP(100) surfaces. Sn doped (n-type, carrier density 1.2×10^{18} cm^{-3}) epiready InP(100) wafers (Crystacomm) were inserted into the vacuum untreated, and cleaned by Ne ion bombardment (20 min at 1 $\mu A/cm^2$, 500 eV) and subsequent 10 min anneal at 350°C.

3. Results

In Fig. 1 we show some representative LEED patterns that were collected from the S-passivated InP(100) surface. The orientation of the wafer is indicated on the figure. After annealing to temperatures below 350°C the surface layer has the 1×1 symmetry of the bulk lattice. This transforms to a 2×1 pattern if the system is annealed in the temperature range 350–500°C. The lowest temperature at which the 2×1 pattern was observed and the quality of the pattern varied from sample to sample, probably as a result of slight differences in the preparation procedure. It should be noted that, on most of the samples studied and in order to reduce the possibility of contamination, LEED measurements were not performed until after the sample had been annealed to 350°C and the photoemission data had been obtained. It is therefore possible that the 2×1 reconstruction occurs also after annealing to lower temper-

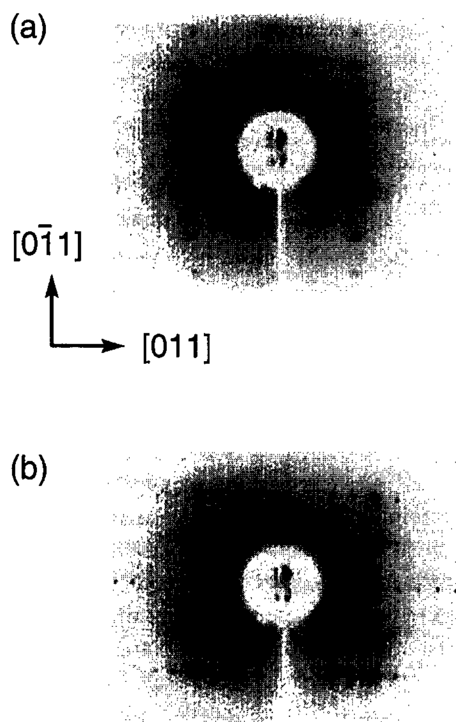

Fig. 1. LEED patterns obtained on InP(100)-S after annealing to (a) 450°C and (b) 500°C. The gun energies are (a) 85 eV and (b) 75 eV. As discussed in the text, the 2×1 pattern was observed after annealing to temperatures in the range 350–500°C. The patterns show a progression in surface symmetry from 2×1 → 2 ×4. This transition has previously been associated with the desorption of S from the surface, although it is also possible that the S diffuses into the bulk. The orientation of the patterns is as illustrated.

atures, but that we simply did not observe it on the few samples that were studied after annealing to these temperatures. The 2 × 1 pattern corresponds to a doubling of the direct lattice spacing along the [0$\bar{1}$1] direction. Annealing to a temperature of approximately 500°C produced a 2 × 4 pattern which is the characteristic phosphorous rich reconstruction seen on InP(100) [12]. Note that the notation used here corresponds to the $\frac{1}{2}$ order spots lying along the [0$\bar{1}$1] direction and the $\frac{1}{4}$ order spots lying along the [011] direction. The appearance of the 2 × 4 pattern after annealing to a temperature near 500°C is consistent with previous work indicating that the S-terminated surface is stable up to this temperature [7,13]. One group [5] reports a stable 2 × 1 reconstruction up to 560°C. The difference may lie in the annealing procedure, since the system is expected to be very sensitive to annealing time once preferential P desorption starts to occur [12]. A 2 × 4 pattern was also obtained on the clean InP(100) surfaces prepared by ion bombardment and annealing to 350°C.

The electronic states near the valence band maximum and conduction band minimum on both the clean 2 × 4 and S-passivated 2 × 1 surfaces were probed at the zone center, $\bar{\Gamma}$, with photoemission and inverse photoemission. In Fig. 2, the results obtained for the two surfaces are compared. The features of the clean surface photoemission spectrum and its position relative to the Fermi level are consistent with results obtained by previous authors [14,15]. The valence band features of the S-passivated surface are shifted to higher binding energy. This indicates a smaller degree of band bending on the S-passivated surface, consistent with the removal of surface states from the gap region. The sharp feature seen at ≈ 1 eV below the Fermi level on the clean

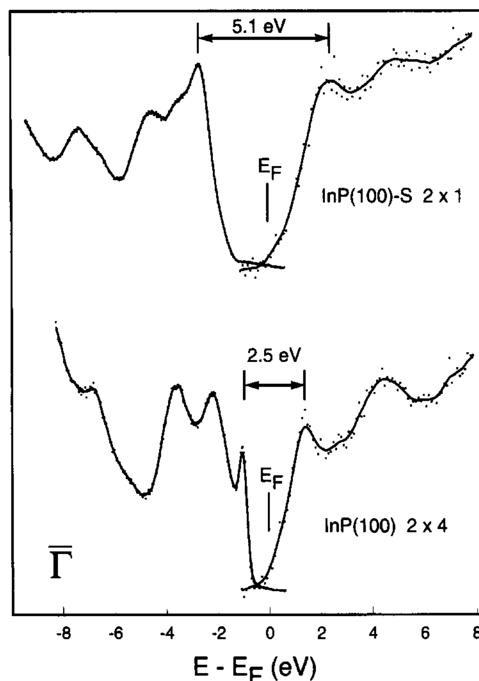

Fig. 2. Photoemission and inverse photoemission spectra obtained in normal emission are shown for InP(100)-S 2×1 and InP(100) 2×4. The alignment of the spectra is discussed in the text. The Fermi level is marked in the figure, but was not used to align the spectra. The surface bandgap is marked in both cases.

surface has been attributed to P dangling bonds [14]. This feature is absent on the S-passivated surface. An unoccupied state near the bottom of the conduction band is also removed by the S-passivation. The unoccupied state is identified as a surface feature since it does not appear on the S-passivated surface. Using a calibration obtained by previous authors [15] of the position of the valence band maximum on the clean 2×4 surface, we find that this unoccupied state lies 2.2 eV above the valence band maximum. This is close to the energy position of an unoccupied state seen on sputter/annealed GaAs(100) 4×2, which has been assigned to Ga dangling bonds [16] (note that the crystallographic directions given by the authors indicate that their 4×2 pattern is equivalent to our 2×4 pattern). It is therefore reasonable that

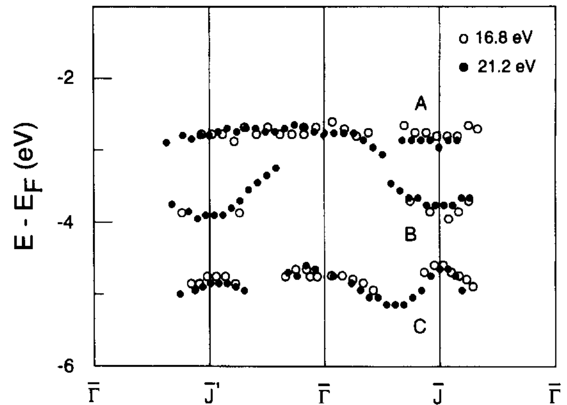

Fig. 4. The dispersion of surface-related features seen on both the 1×1 and 2×1 surfaces of InP(100)-S is plotted along the $\bar{\Gamma}\bar{J}$ and $\bar{\Gamma}\bar{J}'$ directions. The energy is referenced to the Fermi level. The labelling of the features corresponds to the labels used in Fig. 3.

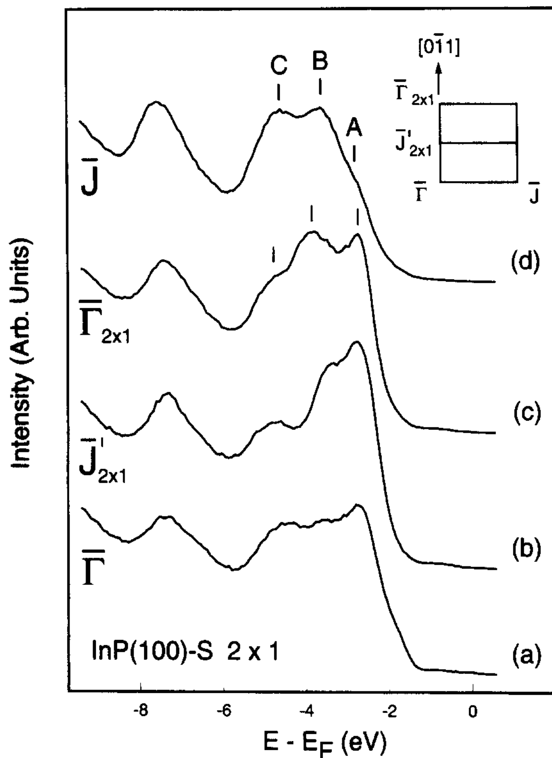

Fig. 3. Photoemission obtained on InP(100)-S 2×1 is shown for several high symmetry points in the surface Brillouin zone. The photon energy is 21.2 eV and the take-off angles are 0°, 12° and 24° respectively along $[0\bar{1}1]$ for (a), (b) and (c). For (d), the take-off angle is 24° along [011]. The angles were chosen such that in each case $k_{\parallel}$ is at the indicated symmetry point for the feature labelled A.

the feature seen on InP(100) 2×4 corresponds to an empty In dangling bond.

On InP(100) 2×4, the surface bandgap at $\bar{\Gamma}$ was found to be 2.5 eV (see Fig. 2), while on InP(100)-S 2×1, it was found to be 5.1 eV. The same results were obtained on a surface of predominantly 1×1 symmetry. It should be noted that we are not measuring the bulk bandgap. Since the photoemission and inverse photoemission experiments were performed at fixed photon energies and not necessarily at an energy where emission from the critical points is observed, the measured gap may be larger than the room temperature bulk bandgap of 1.35 eV [17].

Photoemission measurements were performed on surfaces of both predominantly 1×1 and 2×1 symmetry, along the $\bar{\Gamma}\bar{J}$ and $\bar{\Gamma}\bar{J}'$ directions of the surface Brillouin zone, at photon energies of 21.2 eV (He I) and 16.8 eV (Ne I). No significant differences were noted in the photoemission from the two surfaces, and it has not yet been possible to identify features specifically related to the 2×1 reconstruction. This is perhaps not surprising, since if the 2×1 reconstruction is related to a weak dimerisation, no strong differences are expected [18]. In Fig. 3, spectra obtained at $\bar{\Gamma}$, $\bar{J}'_{2 \times 1}$, $\bar{J}'(\bar{\Gamma}_{2 \times 1})$, and $\bar{J}$ are presented. The features marked have been tentatively identified as surface related. These features are seen at the same binding energy with both photon energies, and exhibit the symmetry of the 1×1 surface Brillouin

zone. The dispersion of the surface related features is shown in Fig. 4. The labelling of the states corresponds to the labels used in Fig. 3. Measurements were also performed along the zone edges [19]. No evidence was found for any bands crossing the Fermi level, indicating that there are no partially filled surface bands.

Assignment of the surface features to particular states awaits a calculation of the surface bands for S-passivated InP(100). The relevant calculations are currently being performed [20]. Qualitatively, one would expect the lower binding energy features to be dangling-bond related, while back bond features should occur at higher binding energies. S dangling-bond features would be expected to occur at a higher binding energy than the P dangling bond feature seen on the clean surface [21].

An interesting similarity is noted between the dispersion of the surface related features reported here and the dispersion of surface features reported for the Ge(100)-S 1 × 1 system [22]. While no assignment of the surface features has been made for either the Ge or InP systems, the comparison is worthy of note. In both cases, a monolayer of S is bonded to the (100) surface of a tetrahedrally coordinated semiconductor, and the lattice constants are similar. The differences in the two systems should be directly related to the difference in valence of the substrate species.

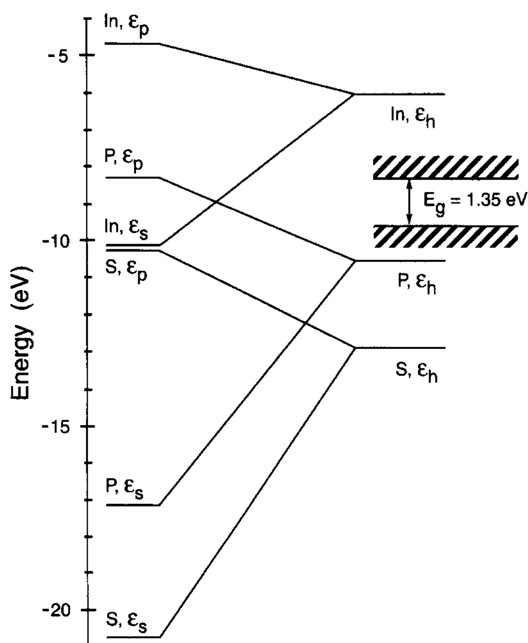

Fig. 5. The energy positions of the In, P and S sp^3 hybrid orbitals are plotted with respect to the valence band maximum and fundamental gap of InP. Hybrid energies were calculated as linear combinations of the energies of the s and p orbitals. The data are from Harrison [21].

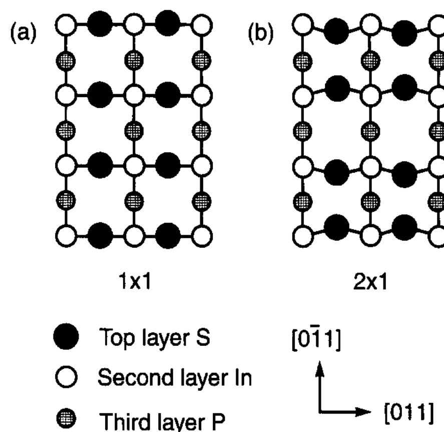

Fig. 6. Simple structural models are shown for (a) InP(100)-S 1 × 1 and (b) InP(100)-S 2 × 1. As is discussed in the text, neither of these models satisfies electron counting.

4. Discussion

As noted above, no evidence was found with photoemission for any surface bands crossing the Fermi level. Therefore the surface is semiconducting and the electron counting model must be satisfied. The electron counting model [23,24] requires that the number of electrons in a semiconductor surface layer is such that all valence band dangling bond states are filled and all conduction band dangling bond states are empty. For the III–V semiconductors, the cation sp^3 dangling bonds lie in the conduction band and the anion sp^3 dangling bonds lie in the valence band. The relative energy positions of the relevant states are shown in Fig. 5 for S, In and P. For the InP(100)-S surface, any S and P dangling bonds should be completely occupied, and any In dangling bonds should be completely empty.

Total energy minimization calculations for S on GaAs(100) [18] and for S on InP(100) [25] have shown that the most energetically favorable adsorp-

tion configuration is one in which the S is bridge-bonded to two In atoms. X-ray photoelectron spectroscopy and Auger electron spectroscopy results indicate that the S coverage on the passivated surface is 1 ML [5,7,26]. Both 1×1 [26] and 2×1 [5,7] patterns have been observed with LEED and RHEED. The simplest models that might account for these observations are shown in Fig. 6. These models are consistent with the diffraction data, and dimer formation, as postulated for the 2×1 reconstruction, is common on the (100) surfaces of tetrahedrally coordinated semiconductors (see e.g. [27]). However, neither of these structures satisfies electron counting.

In order to apply the electron counting model to the InP(100) surface, we assume that an In atom (valence 3) contributes $\frac{3}{4}$ of an electron to each of its four sp^3 hybrids, and that a P atom (valence 5) contributes $\frac{5}{4}$ of an electron to each of its four sp^3 hybrids. One is then able to count up the number of electrons available per surface unit cell and to compare this number with the number required to fill the appropriate dangling bond orbitals.

We will first consider the case of 1 ML of S bridge-bonded to In, corresponding to the postulated 1×1 structure [26]. The electron counting model requires that all of the S dangling bonds be completely occupied. There is one S atom per surface unit cell. $2\frac{1}{2}$ of its six electrons are required for bonding to the top layer of In atoms. There are $3\frac{1}{2}$ electrons left over to fill the two dangling bonds per unit cell. However, four electrons are needed to saturate the dangling bonds. Consequently, the electron counting model is not satisfied.

A similar argument can be applied to the 2×1 model, in which the S atoms are assumed to form dimers along the $[0\bar{1}1]$ direction. Again, the electron counting model requires that all of the S dangling bonds be completely occupied. There are now two S atoms per surface unit cell. Five electrons are required for bonding the two S atoms to the top layer of In atoms. There are seven electrons left over to fill the dimer bond and the two remaining S dangling bonds. Only six are required. Again, the electron counting model is not satisfied.

In order to satisfy the electron counting model for a 1 ML coverage of S atoms bridge bonded to In (whether dimerized or not), either P or In vacancies must be introduced in subsurface layers. If the S coverage is greater than 1 ML, structures satisfying the electron counting model can be found by replacing some of the third layer P atoms by S. A structure of this type has been proposed for the system GaAs(001)-Se 2×1, in which the electron counting considerations are the same as for sulfur on InP(100) [28].

We note that the electron counting model can be naturally satisfied if the surface layer comprises only half a monolayer of P atoms and half a monolayer of S atoms. In this case the formation of S–P dimers saturates the S and P dangling bond orbitals. As before, the S contributes $2\frac{1}{2}$ electrons to surface bonds and has $3\frac{1}{2}$ left over. The P contributes $2\frac{1}{2}$ electrons to surface bonds and has $2\frac{1}{2}$ left over. The S–P dimer then has a full complement of six electrons with which to fill the dimer bond and the two dangling bonds. Attractive as this possibility is, there is little experimental evidence that the overlayer comprises 0.5 ML of S, at least for surfaces annealed at temperatures less than 500°C. However, a previous study [5] found 0.5 ML S remaining on a well-ordered 2×1 surface after annealing to 560°C, and the S–P dimer structure was suggested as a possible surface model.

Several experiments on S-passivated InP(100) (for example Ref. [5]), indicate that at least after annealing to 350°C, S is present in the third layer, in bulk P positions. Thermodynamically, the P–S exchange is favored [5]. Thus, there are good reasons for incorporating some subsurface S in any proposed structural model. If the S coverage is close to 1 ML as suggested by the experiments performed to date, then a structure satisfying electron counting would naturally include both subsurface vacancies and subsurface S.

As noted above, the surface electronic features on S-passivated Ge(100) and InP(100) are strikingly similar. An obvious difference between the two systems is that in the case of Ge(100), the tetravalent Ge atoms allow the simple bridge-bonded 1×1 S overlayer to satisfy the electron counting model. On InP(100)-S, a more complicated reconstruction is required to satisfy this model. Since the substrate structure and adsorption sites are the same, however, it is not surprising that the resulting electronic structures are similar. One of the features that makes the InP(100)-S system especially interesting is the 1×1

→ 2 × 1 transition. This transition indicates the existence of an activation barrier [3] which may be related to S incorporation in subsurface layers and/or to the formation of subsurface vacancies.

Acknowledgements

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