Photoelectron bandstructure of InP(110)-Sb monolayers

1991 J. Phys.: Condens. Matter 3 S367

(http://iopscience.iop.org/0953-8984/3/S/057)

J. Phys.: Condens. Matter 3 (1991) S367–S372. Printed in the UK

Photoelectron bandstructure of InP(110)–Sb monolayers

I T McGovern†, R Whittle†, D R T Zahn‡, C Müller‡, C Nowak‡, A Cafolla§ and W Braun¶

† Department of Pure and Applied Physics, Trinity College, Dublin, Ireland
‡ Institut für Festkörperphysik, Technische Universität, Hardenbergstrasse 36, D-1000, Berlin 12, Federal Republic of Germany
§ Department of Physics, University of Wales College of Cardiff, PO Box 913, Cardiff CF1 3TH, UK
¶ BESSY, Lentzeallee 100, D-1000 Berlin 33, Federal Republic of Germany

Received 25 April 1991

Abstract. The electronic bandstructure of an ordered 1 × 1 overlayer of Sb on InP(110) has been investigated by angle-resolved photoelectron spectroscopy using synchrotron radiation. The experimental energy dispersion of the features in the spectra has been mapped along high-symmetry directions in the surface Brillouin zone. An analysis based on a number of criteria is employed to distinguish surface-related features and these are compared with a 'tight-binding, total energy minimization' calculation based on a zig-zag chain model of Sb on the InP(110) surface. Two bands near the valence band maximum are found to be in reasonable agreement with predicted states with a bonding character associated with the adsorption on anion and cation sites. The nature of two further bands at higher binding energy is discussed.

1. Introduction

The adsorption of group V atoms onto the cleavage face of III–V semiconductors is known to provide a (1 × 1) ordered overlayer (Duke *et al* 1982). These systems are of interest within Schottky barrier research as they offer the possibility of ordered, abrupt and non-reactive interfaces (Stephens *et al* 1990). In this paper the surface electronic bandstructure of the Sb–InP system is investigated by angle-resolved photoelectron spectroscopy using synchrotron radiation. Various criteria are applied to distinguish the surface electronic bandstructure and these are compared with the predictions of the tight-binding, total energy minimization calculation of Mailhiot *et al* (1985). A schematic diagram of the side and top views of the adsorption geometry employed in that calculation is shown in figure 1(*a*): this model, in which the Sb atoms form a zig-zag chain bonded to a nearly unrelaxed (110) substrate, is known as the epitaxial continued layer structure (ECLS) (LaFemina *et al* 1990). The surface Brillouin zone (SBZ) of this structure is shown in figure 1(*b*).

2. Procedure

The measurements were performed on a VG Ltd ADES 400 spectrometer at the TGM 2 beamline of the electron storage ring in Berlin (BESSY). Full details of the experimental

apparatus and methods are to be found in Stephens *et al* (1990). In addition, it has been shown that a more 'perfect' first layer (i.e. exactly one Sb adatom for each In and each P atom) is formed by annealing an excess deposit to 600 K (Whittle *et al* 1991) and this preparation was employed here. A work function of 5.3 eV for Sb/InP was measured by applying a negative voltage to the sample and measuring the cutoff of secondary electrons.

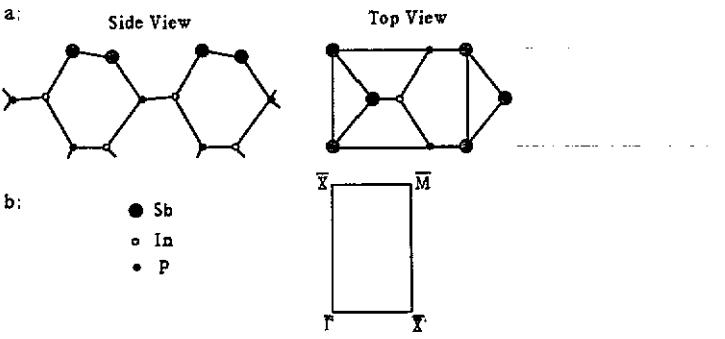


Figure 1. (*a*) Schematic diagram of side and top views of the ECLS model of Sb on InP(110), (*b*) the surface Brillouin zone of this structure.

In all reported measurements the light beam was incident at 45° to the surface normal with the polarization vector lying in the plane of the surface normal and the $\bar{\Gamma}$–$\bar{X}$ direction of the SBZ. The polar angle of emission θ_e is the angle between the outgoing electron and surface normal and the azimuthal direction is specified by the projection of the emission onto the SBZ. Thus, the $\bar{\Gamma}$–$\bar{X}$ and $\bar{\Gamma}$–$\bar{X}'$ spectra are 'in plane' and 'out of plane', respectively.

3. Results

Figure 2 shows a typical set of spectra, showing the dispersion of features along the $\bar{\Gamma}$–$\bar{X}$ direction in the SBZ at a photon energy of 19 eV; the angle mesh is 2.5°. Additional sets were taken at a photon energy of 21.2 eV and for the same two photon energies along the $\bar{\Gamma}$–$\bar{X}'$ direction. From these sets peak energies relative to the vacuum level are convoluted with an angle to yield the composite k-parallel plots shown in figure 3(*a*) for $\bar{\Gamma}$–$\bar{X}$ and figure 3(*b*) for $\bar{\Gamma}$–$\bar{X}'$. The full symbols correspond to well defined peaks and the open symbols to lesser peaks or shoulders; the data for 19 and 21.2 eV photon energies are shown as squares and circles, respectively. Also shown on these plots is the portion of the so-called 'stomach gap' in the projection of the bulk bands in the regions of $\bar{X}$ and $\bar{\Gamma}$–$\bar{X}'$, as calculated by Srivastava *et al* (1983). This calculation yields a smaller stomach gap than that of Mailhiot *et al* (1985). This gap is material to one of the criteria for determining surface-related features in figure 3.

Plummer and Eberhard (1982) discuss two criteria for surface states, namely (1) the state must lie in a gap in the projection of the bulk bandstructure onto the SBZ and (2) its $k_{\|}$ dispersion should be independent of photon energy. In order to distinguish the surface-related features in figure 3, these criteria are combined with a third, namely

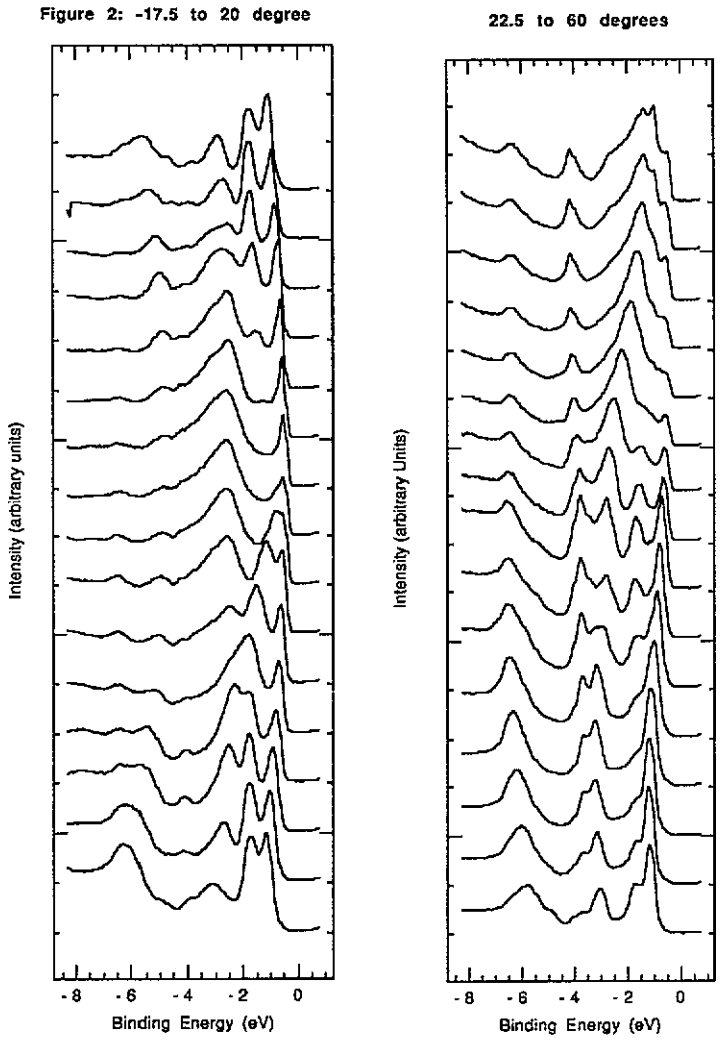
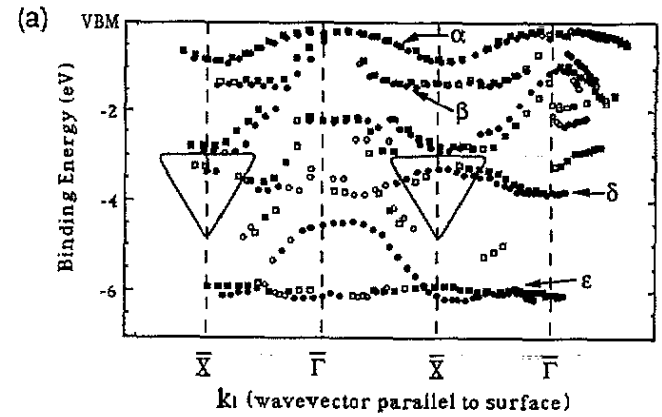


Figure 2. Angle-resolved photoelectron spectra for Sb–InP(110) along $\bar{\Gamma}$–$\bar{X}$ at photon energy of 19 eV, every 2.5° between polar angles of −17.5 and 60°.

that the dispersion should repeat along the $\bar{\Gamma}$–$\bar{X}$–$\bar{\Gamma}$ and $\bar{\Gamma}$–$\bar{X}$–$\bar{\Gamma}$ directions. The first criterion may be relaxed for the adsorbate-related structure here but it does provide a 'sufficient case' if part of the band meets this criterion. Application of these criteria indicates that there are four bands which may be tentatively described as surface-related. These are reproduced in figure 4 where they are labelled α, β, δ and ϵ. This labelling is employed because different labelling of surface features has been used in experiment (Martensson *et al* 1986) and calculations (Mailhiot *et al* 1985, Bertoni *et al* 1983).

The strongest case can be made for the band labelled α. This band is visible at almost all points along $\bar{\Gamma}$–$\bar{X}$ except near $\bar{\Gamma}$. Along $\bar{\Gamma}$–$\bar{X}'$ the signal is more difficult to see, partly because of the out-of-plane geometry. The dispersion repeats well and the two photon energies have a good overlap. When transferred to figure 4, portions of this band lie outside the projected bulk bands (Mailhiot *et al* 1985).



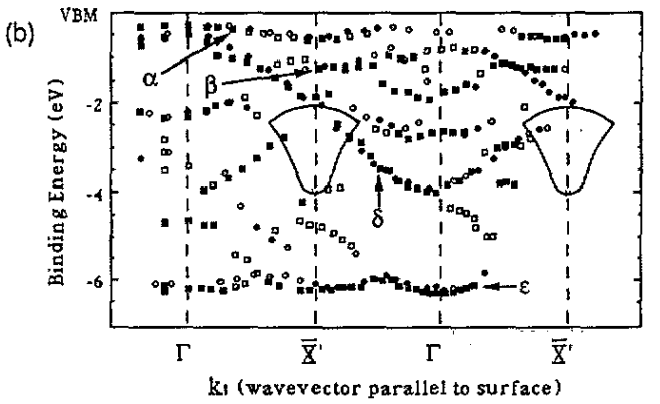


Figure 3. Composite k-parallel plots along (*a*) $\bar{\Gamma}$–$\bar{X}$ and (*b*) $\bar{\Gamma}$–$\bar{X}'$ directions of the SBZ.

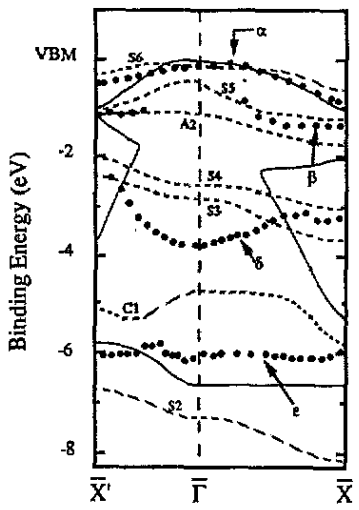


Figure 4. Comparison of experimental bands with the calculation of Mailhiot *et al* (1985) along the directions $\bar{\Gamma}$–$\bar{X}$ and $\bar{\Gamma}$–$\bar{X}'$.

The band labelled β also exhibits good overlap at the two photon energies. However, this band is less clear than α in both symmetry directions, being stronger at $\bar{X}$ and $\bar{X}'$ than at Γ. This may be because it always lies in the projection of the bulk bands, as indicated by calculations of both Mailhiot *et al* (1985) and Srivastava *et al* (1983). Between band β and the next band δ there are many features which are interpreted as bulk states; these largely fall inside the 'stomach gap' of Mailhiot *et al* (1985) but not in the corresponding smaller gap of Srivastava *et al* (1983). In this respect our data support the latter calculation. The band labelled δ is fairly easy to identify along $\bar{\Gamma}$–$\bar{X}'$ direction; the dispersion repeats well and there is good overlap of the two photon energies. This is a strongly dispersing band. Its companion along $\bar{\Gamma}$–$\bar{X}$ is less convincing, partly because it is obscured by other features throughout much of the SBZ. However, near the X point along $\bar{\Gamma}$–$\bar{X}$ this band enters well inside the stomach gap of both sets of calculations, confirming that it is a surface-related feature.

The band labelled ϵ, the lowest in energy, shows minimal dispersion throughout. Sorba *et al* (1987) report a similar feature in the spectra of the clean InP(110) surface. In that work this feature was shown not to disperse in k-perpendicular either; this invalidated the use of the second criteria of Plummer and Eberhard (1982). However, it does appear to repeat within its limited dispersion and it just extends beyond the bulk bands projection near $\bar{X}'$. For completeness, it is included in figure 4.

4. Discussion

The four experimental bands are plotted onto the surface and bulk bandstructure calculated by Mailhiot *et al* (1985) in figure 4. This is to our knowledge the only published calculation for Sb–InP(110) and is part of a family of Sb on III–V (110) surfaces; Bertoni *et al* (1983) have calculated Sb–GaAs(110) and Martensson *et al* (1986) have provided a photoelectron bandstructure for that system.

In Mailhiot *et al* (1985) the surface bands are labelled S1 to S6 with decreasing binding energy. In figure 4 the experimental bands have been rigidly shifted upward by approximately 0.45 eV, so that α and S6 are aligned at Γ; this is not unreasonable given the usual degree of band bending. There is reasonable agreement in the dispersion of band α and S6. The binding energy of the band β agrees well with that of S5 but the dispersion is not as closely matched. In this calculation these two bands are associated with bonding of the Sb chain to the substrate, at the In(S6) and P(S5) atom sites.

Of the remaining experimental bands, band ϵ lies median between C1, which is a cation-derived surface state, and S2, which is s-like in origin. However, its surface provenance is not strong. The band δ may be compared with S3/S4 manifold of the calculation. Although there is good agreement in binding energy at X and X′, the discrepancy reaches about 1 eV at Γ. These states correspond to p^2 bonding within the Sb chain. It is not clear what adjustment of the geometric model would address this discrepancy. Recently, LaFemina *et al* (1990) have extended this calculation to a second model known as the 'epitaxial on top structure' (EOTS) in which the Sb chains are commensurate with the Ga–As chains. There are lattice-mismatch arguments which suggest that this model would be more appropriate for Sb–InP(110). However, comparison of the surface bandstructures calculated for Sb–GaAs(110) does not materially alter the S3/S4 manifold, which is not unexpected given the origin of these bands in the Sb layer; in fact, the EOTS calculation lowers the overall dispersion of S5 and S6 which, assuming transferability to InP, would only create a greater discrepancy with the experimental band α.

5. Conclusion

This photoelectron spectroscopy investigation of the surface electronic bandstructure of Sb–InP(110) has revealed four bands which have surface provenance in varying degrees. The upper two bands are in reasonable agreement with calculated bands associated with bonding between the Sb chain and the substrate. Of the other two bands, for which there is less agreement with the calculation, one may have a bulk origin and the other may be indicative of a model other than the ECLS and EOTS which have been calculated to date. It is intended to investigate polarization effects for this system in a further publication (Whittle *et al* 1992).

Acknowledgments

ITMcG and RW acknowledge the support of the Large Installations Plan through DG IIX of the European Community. D Everly is thanked for assistance with the typing of this manuscript.

References

Bertoni C M, Calandra C, Manghi F and Molinari E 1983 *Phys. Rev.* B **27** 1251

Duke C B, Paton A, Ford W K, Kahn A and Carelli J 1982 *Phys. Rev.* B **26** 803

LaFemina J, Duke C B and Mailhiot C 1990 *J. Vac. Sci. Technol.* B **4** 888

Mailhiot C, Duke C B and Chadi C H 1985 *Phys. Rev.* B **31** 2213

Martensson P, Hansson G V, Laehdeniemi M, Magnusson K O, Wiklund S and Nicholls J M 1986 *Phys. Rev.* B **33** 7399

Plummer E W and Eberhard W 1982 *Adv. Chem. Phys.* **49** 533

Sorba L, Hinkel V, Middelmann H U and Horn K 1987 *Phys. Rev.* B **36** 8075

Srivastava G P, Singh I, Montgomery V and Williams R H 1983 *J. Phys. C: Solid State Phys.* **16** 3627

Stephens C, Zahn D R T, Fives K, Cimino R, Braun W and McGovern I T 1990 *J. Vac. Sci. Technol.* B **8** 674

Whittle R, McGovern I T, Zahn D R T, Muller C and Braun W 1991 *BESSY Annual Report 1990* (Berlin: BESSY) p 323

—— 1992 *Proc. ICFSI-3, Rome (1991)* to be published in *App. Surf. Sci.*