

## Electronic Band Structure of Monolayer Bi on GaP(110)

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(Received 22 May 1995; accepted 18 July 1995)

The two-dimensional electronic band structure of monolayer Bi on GaP(110) has been mapped using angle-resolved UV photoelectron spectroscopy (ARUPS) with synchrotron radiation. Surface photovoltage effects are corrected for by simultaneous second-order core spectroscopy. From valence-band spectra along the four symmetry directions of the surface Brillouin zone at three photon energies it is possible to distinguish three states as surface related. The topmost band is found to be inside the fundamental band gap, at *ca* 0.75 eV above the bulk valence-band maximum. Comparison with other V/III–V(110) systems shows that this system is not significantly different, despite the relatively large size of the Bi atoms with respect to the GaP lattice; in a selective comparison with InP and GaAs it would appear that Bi-substrate anion bonding is a more important factor than strain.

**Keywords:** photoelectron spectroscopy; ARUPS; semiconductor interfaces; Bi on GaP(110).

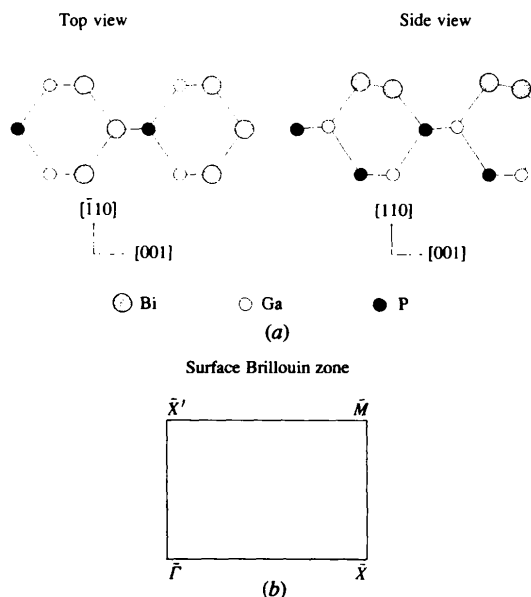
### 1. Introduction

The adsorption of Sb and Bi atoms onto the (110) surface of III–V semiconductors is of particular interest to Schottky barrier research because most of these systems are known to produce ordered (1 × 1) monolayers which are stable and non-reactive (Ford, Guo, Lantz *et al.*, 1990). A schematic diagram of the side and top views of the favoured model

of the majority of these systems is shown in Fig. 1(a). The group V atoms form a zigzag chain along the surface, taking up positions similar to those of the respective III and V atoms, the ‘epitaxial continued layer structure’ (LaFemina, Duke & Mailhot, 1990). The surface Brillouin zone (SBZ) is shown in Fig. 1(b).

The large number of similar overlayer/substrate combinations available makes these systems ideal candidates for systematic study, *e.g.* of the relative effects of strain and interface bonding on overlayer growth and electronic structure. Of all these interfaces Bi:GaP represents the largest strain which is here defined as the ratio of overlayer covalent radius to half the substrate lattice constant. It might then be expected that Bi/GaP should demonstrate the most pronounced effects of strain. Indeed, a LEED study has reported a 6 × 1 pattern and STM studies have shown that the Bi chains along the  $[\bar{1}00]$  direction grow to only 6–8 atoms in length before forming dislocations (Prietsch, Samsavar & Ludeke, 1991). This is similar to Bi/GaAs, in which the chains are *ca* 10–11 atoms long (Ludeke, Taleb-Ibrahimi, Feenstra & McLean, 1989). However, an XSW study was unable to establish an overlayer geometry because of the lack of long-range order (Herrera-Gómez *et al.*, 1994).

In this work the surface electronic band structure of the Bi/GaP(110) system is investigated by angle-resolved photoelectron spectroscopy (ARUPS) using synchrotron radiation. Surface-related bands are identified along the four principal symmetry directions of the SBZ and comparison is made with ARUPS studies of similar systems.



**Figure 1**  
Schematic diagram of (a) proposed surface geometry, and (b) surface Brillouin zone.

## 2. Procedure

The measurements were performed using a VG Ltd ADES 400 angle-resolved spectrometer with angular resolution of  $4^\circ$  at the TGM2 beamline of the electron storage ring in Berlin (BESSY). Clean surfaces of  $n$ -GaP(110) ( $n = 4.4 \times 10^{17} \text{ cm}^{-3}$ ) were prepared by cleaving in ultra-high vacuum. Bi was evaporated *in situ* from a Knudsen-type cell made of tantalum foil. The thickness of the Bi deposit was monitored by quartz-crystal oscillators and by observing the different components of the Bi 5*d* core levels. The Bi monolayer was formed by annealing an excess deposit of 3–5 monolayers to *ca* 500 K. After annealing LEED showed a  $1 \times 1$  pattern.

The spectra from these samples, even after the completion of an annealed Bi monolayer, showed variable shifts of up to 0.7 eV, depending on the light intensity. These shifts can be attributed to the surface-photovoltage effect, which has previously been observed on many metal/III–V(110) semiconductor interfaces, and is particularly pronounced for large bandgap GaP (Alonso, Cimino & Horn, 1990; Hecht, 1990). The presence of surface photovoltage hinders the accurate measurement of the sample Fermi level, and thus poses a problem for alignment of spectra since shifts due to surface photovoltage are not readily distinguished from those due to dispersion. To overcome this problem the valence spectra were taken at photon energies which permitted simultaneous measurement of substrate/overlayer core levels, excited by second- or higher-order light. Spectra can then be aligned along these core levels allowing the binding energy  $E_b$  of valence features to be calculated with respect to the bulk valence-band maximum (VBM), measured from the clean sample surface.

Dispersion is calculated from the kinetic energy relative to the sample vacuum level. A work function of 3.4 eV for Bi/GaP was established by applying a negative voltage to the sample and measuring the cut-off of secondary electrons. This measurement is also hindered by the presence of surface photovoltage, and this value for the work function should be considered as a (somewhat) adjustable parameter which can be tuned so that the dispersion of surface features repeats itself upon translation of a surface reciprocal lattice vector.

Surface-related features are identified on the basis of criteria developed for surface states (Plummer & Eberhart, 1982), namely that  $k$ -parallel dispersion is independent of photon energy and that the state resides in a gap in the projection of the bulk band structure onto the SBZ. This second criterion may be met only in a portion of the SBZ and no formal distinction is made between surface states and surface resonances.

## 3. Results

Spectra were taken along each of the four symmetry directions at photon energies of 14, 20 and 28 eV. Typical spectra taken at  $h\nu = 28 \text{ eV}$  along the  $\bar{\Gamma} - \bar{X}'$  symmetry direction of the SBZ are shown in Fig. 2. The spectra have been

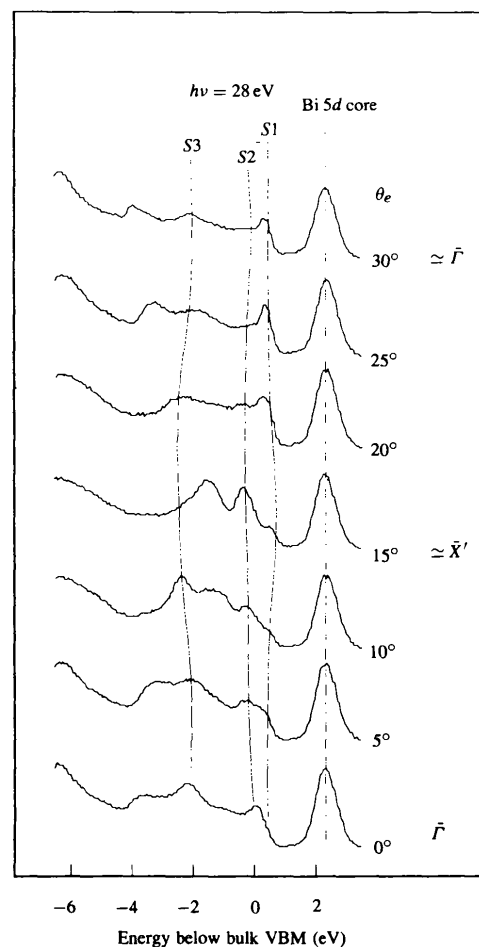
aligned along the Bi-5*d* core level, excited by second-order light, as previously discussed.

For each set of spectra, peak-energy positions are plotted against the momentum component in  $\text{\AA}^{-1}$  parallel to the surface ( $k_{\parallel}$ ) using

$$k_{\parallel} = 0.51(E_{\text{kin}} \sin \theta_e)^{1/2}$$

where  $E_{\text{kin}}$  is the kinetic energy of the photoemitted electron relative to the vacuum level in eV and  $\theta_e$  is the angle of the emitted electron with respect to the surface normal.

Plots of  $E_b$  versus  $k_{\parallel}$  for three photon energies (14, 20 and 28 eV) along each symmetry direction of the SBZ are shown in Fig. 3. Also shown on these plots is the projection of the GaP bulk band structure onto the (110) surface from a calculation by Alves, Hebenstreit & Scheffler (1990). For the  $\bar{X} - \bar{M}$  and  $\bar{X}' - \bar{M}$  directions of the SBZ,  $k_{\parallel}$  is only precisely located on these symmetry lines at one kinetic energy within a given energy distribution curve; however, in these plots the value of  $k_{\parallel}$  deviates by less than 5% from the symmetry lines. Using the criteria described earlier, three states labelled S1–S3 can be identified as being of surface origin. S1 and S2 are degenerate throughout most of the



**Figure 2**  
Sample spectra along the  $\bar{\Gamma} - \bar{X}'$  direction of the SBZ. The spectra are aligned along the Bi-5*d* core level peaks resulting from second-order light.

SBZ, and lie above the projection of the bulk valence bands.  $S1$  reaches its highest energy at  $\bar{X}'$  where it is *ca* 0.75 eV above the bulk valence-band maximum.  $S3$ , which is not visible along  $\bar{\Gamma} - \bar{X}$ , is mainly found inside the projection of the bulk bands except near  $\bar{X}'$ . This state is the most dispersive of the three states rising 1.85 eV from  $\bar{\Gamma}$  to  $\bar{X}'$ . The composite dispersion of these states is shown in Fig. 4.

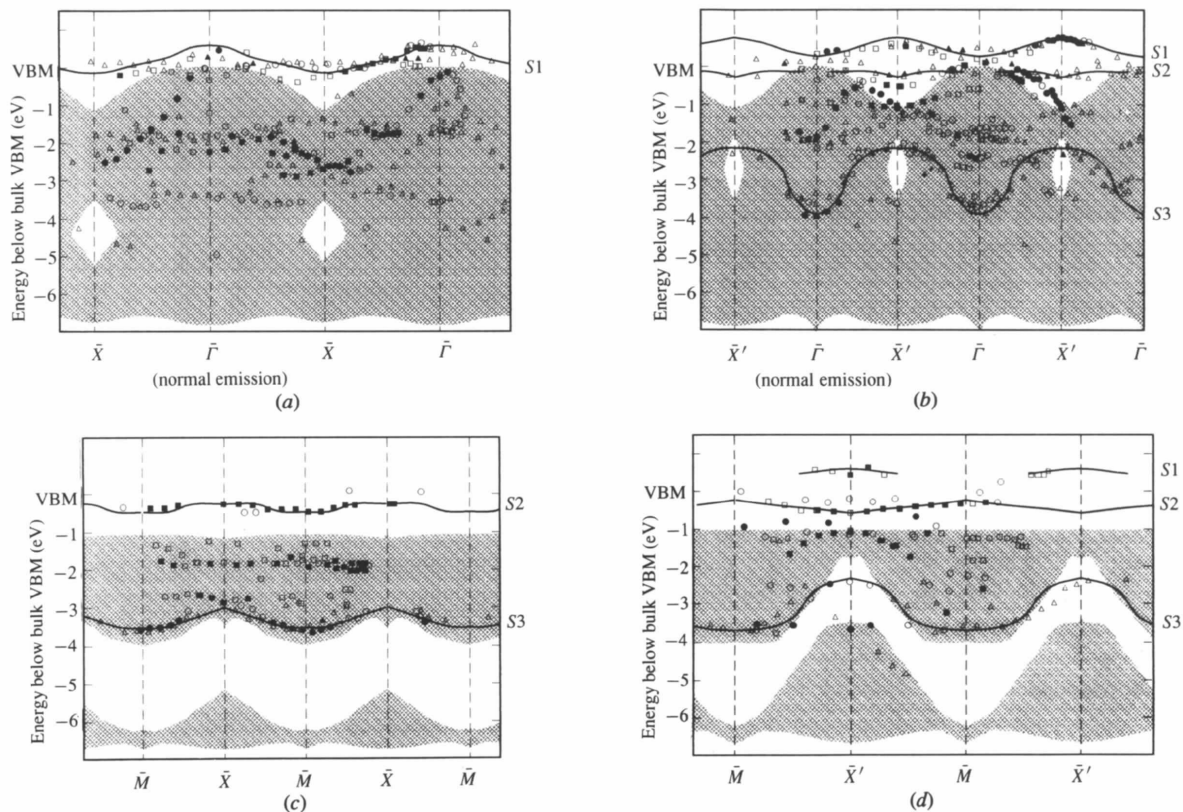
#### 4. Discussion

Perhaps the first point to note is that the surface electronic structure seems to be well developed, clearly repeating with the SBZ corresponding to the  $(1 \times 1)$  unit cell. Although Bi forms only a quasi-ordered overlayer (Prietsch *et al.*, 1991), the electronic band structure reflects the shorter range order. Furthermore, qualitative comparison with the reported surface band structures for similar systems indicates that this system is well within the range exhibited by this family, suggesting that the overlayer geometry of this system is similar to the others, namely the epitaxial continued layer structure given in Fig. 1.

In the absence of a reliable calculation for detailed comparison, the discussion of this system is widened to attempt some comparison of related systems on the basis of overlayer strain and/or interface bonding. Although the reported number of observed surface-related states varies

with the system, states corresponding to those labelled  $S1$  and  $S3$  in this study are common to all of them. In Table 1 the surface state bandwidths along some SBZ lines are tabulated along with the location and energy of the maximum of the topmost state ( $S1$ ). In this table strain has been defined as the covalent radius of the overlayer atom divided by half the substrate lattice constant. Although it would be reasonable to expect that increased strain might lead to greater orbital overlap and hence a larger bandwidth, the table shows no obvious trends in this regard. Nor does the energy or location (in the SBZ) of the topmost state seem particularly dependent on overlayer strain. One possible trend which might be noted is that the dispersion of  $S3$  along  $\bar{\Gamma} - \bar{X}'$  shows some correlation with the substrate lattice constant. With the exception of Bi/InAs the bandwidth of this state appears to grow with decreasing lattice constant.

A more viable correlation may be apparent within the Bi grouping, in particular for the sub-group of Bi/GaP, Bi/GaAs and Bi/InP. For this sub-group the variable is the substrate anion or cation species. In these three systems the state corresponding to  $S3$  is very similar in terms of both dispersion and bandwidth. It can be concluded that this state probably has a similar orbital character and no further trend is evident. Comparison of  $S1$  (the most weakly bound state in each case) shows that the principal differences between

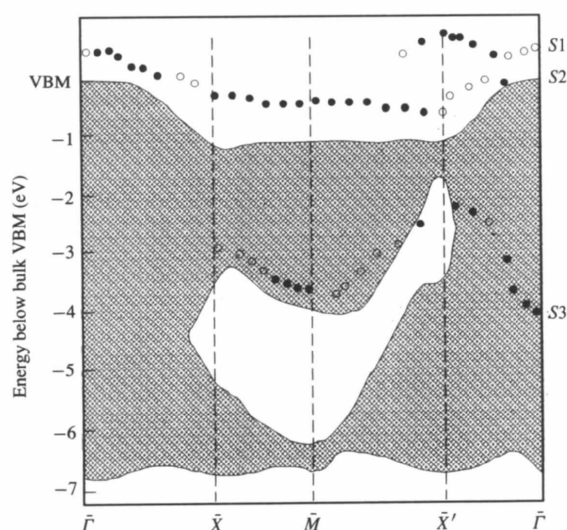


**Figure 3**

Composite  $E_b$  versus  $k_{\parallel}$  plots along (a)  $\bar{\Gamma} - \bar{X}$ , (b)  $\bar{\Gamma} - \bar{X}'$ , (c)  $\bar{X} - \bar{M}$  and (d)  $\bar{X}' - \bar{M}$ . Squares, circles and triangles correspond to photon energies of 14, 20 and 28 eV, respectively. Filled symbols represent strong spectral features, empty symbols represent weak features or shoulders. The shaded region corresponds to the projection of the bulk band structure of Alves *et al.* (1991). Surface bands are highlighted with a continuous line.

the systems are (i) the position of this state relative to the bulk valence-band maximum, and (ii) the location in the SBZ at which this state is at its highest energy, *i.e.* whether it disperses up or down from  $\bar{\Gamma}$  to  $\bar{X}'$ . With respect to the first point,  $S1$  is furthest inside the bulk bandgap for Bi/GaP (0.75 eV) followed by Bi/GaAs (0.54 eV) and then Bi/InP (0.45 eV). This trend is in keeping with the relative strain for the three interfaces but whether there is a formal connection is unclear.

On the second point of comparison, for Bi/InP and Bi/GaP  $S1$  disperses upwards from  $\bar{\Gamma}$  to a maximum at  $\bar{X}'$  while for Bi/GaAs  $S1$  disperses from its maximum at  $\bar{\Gamma}$  downward to  $\bar{X}'$ . This difference cannot be accounted for simply in terms of geometry or strain, since LEED studies have concluded that both Bi/GaAs and Bi/InP have the same (epitaxial continued layer structure) geometry (Ford, Guo, Lessor & Duke, 1990; Ford, Guo, Wan & Duke, 1992), and strain arguments would imply that Bi/GaP should be more like Bi/GaAs than Bi/InP. In a simple tight-binding picture opposite signs of dispersion imply different symmetry states. However, neither this experiment or available calculations provide any information on symmetry. A more available candidate is the different bonding of the interface, particularly involving the substrate anion. In a tight-binding calculation of the Bi/InP interface (Whittle, 1994), it was found that  $S1$  was primarily made up of Bi–Bi overlayer bonds lying largely in the plane of the Bi–Bi chains and with very little bonding to the substrate. In a separate tight-binding study of the Bi/GaAs interface (Bowler, Hermanson, LaFemina & Duke, 1992, 1993) the corresponding state was found to be made up principally of orbitals lying perpendicular to the surface, presumably involving bonding to the substrate. These results suggest that the difference may be accounted for by interaction of the Bi chain with the substrate, and since the electronic structure of Bi/GaP is



**Figure 4**  
Experimental bands along the four SBZ directions. The shaded regions correspond to the projection of the bulk band structure of Alves *et al.* (1991). Filled symbols represent strong spectral features, empty symbols represent weak features or shoulders.

**Table 1**

Summary of the dispersion characteristics of similar states in V/III–V(110) interfaces.

Interface	Lattice constant (Å)	Strain	$S1$ $\bar{\Gamma} - \bar{X}$ (eV)	$S1$ $\bar{\Gamma} - \bar{X}'$ (eV)	$S3$ $\bar{\Gamma} - \bar{X}'$ (eV)	$S1 >$ VBM (eV)	$S1$ max. at	Ref.
Bi/GaP	5.451	1.238	0.73	0.35	1.85	0.75	$\bar{X}'$	(1)
Bi/GaAs	5.654	1.196	0.98	0.83	1.40	0.54	$\bar{\Gamma}$	(2)
Bi/InP	5.869	1.15	0.83	0.68	1.40	0.45	$\bar{X}'$	(3)
Bi/InAs	6.036	1.118	0.60	0.20	0.79	$\leq 0$	$\bar{X}'$	(4)
Bi/GaSb	6.118	1.104	1.09	0.31	1.31	$\leq 0$	$\bar{\Gamma}$	(5)
Sb/GaP	5.451	1.182	0.63	0.05	1.84	$\leq 0$	$\bar{X}'$	(6)
Sb/GaAs	5.654	1.141	1.05	0.45	1.60	$\leq 0$	$\bar{\Gamma}$	(7)
Sb/InP	5.869	1.099	0.73	0.37	1.46	$\leq 0$	$\bar{\Gamma}$	(8)

In each case  $S1$  corresponds to the most weakly bound surface state and  $S3$  to the state predominantly observed in the mid-band gap in the surface projection of bulk states (the so-called stomach gap). The strain is defined as the covalent radius of Bi or Sb divided by half the substrate lattice constant. The third, fourth and fifth columns correspond to the bandwidth of a given state along the indicated SBZ line and the last two columns correspond to the maximum energy above the bulk valence-band maximum (VBM) of  $S1$  and the location of this maximum in the SBZ. The label  $\leq 0$  indicates that this state remains below or at the bulk VBM. (1) This work. (2) McLean *et al.* (1991). (3) Whittle *et al.* (1993). (4) McIlroy, Heskett, Swanston *et al.* (1993). (5) McIlroy, Heskett, McLean *et al.* (1993). (6) Whittle *et al.* (1994). (7) Mårtensson *et al.* (1986). (8) Whittle *et al.* (1992).

more like that of Bi/InP than Bi/GaAs, it may be inferred that the important distinction between the systems is the interaction of Bi with the substrate anion (group V atom).

## 5. Conclusions

An ARUPS study of  $(1 \times 1)$  monolayer Bi on GaP(110) finds three surface-related bands. Two reside inside the fundamental bulk gap of the substrate and the third enters the mid-band gap in the surface projection of bulk states (the so-called stomach gap). Comparison with other V/III–V interfaces indicates that this Bi overlayer system is broadly similar to these other interfaces. This comparison suggests that the larger strain of this overlayer is not strongly reflected in the band structure. A more selective comparison with InP and GaAs suggests that Bi-substrate anion bonding may be a more important factor than strain.

ITMcG, AM, ED and RW acknowledge the support of the Large Installations Plan through DG XII of the European Community.

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