Surface core-level shifts for the (110) cleavage face of III-V semiconductors: InAs(110)

LETTER TO THE EDITOR

Surface core-level shifts for the (110) cleavage face of III–V semiconductors: InAs(110)

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Abstract. The lineshapes of the In 4d and As 3d core-levels on InAs(110) have been studied using least squares analysis and the surface core-level shifts are found to be $+0.28 \pm 0.02$ and -0.30 ± 0.02 eV respectively. Consequently, the surface core-level shifts have now been determined for the entire family of III–V semiconductor surfaces which includes GaX(110) and InX(110), where X = P, As and Sb. It is shown that the quantity $\Delta E_C - \Delta E_A$, where ΔE_C is the cation surface core-level shift and ΔE_A is the anion surface core-level shift, exhibits a systematic dependence upon the semiconductor ionicity.

Although core-level photoelectron spectroscopy is widely used in the study of III–V semiconductor surfaces and interfaces, it is still unclear which of the contributing factors to the surface core-level shift is the most important on the natural (110) cleavage plane [1]. However, the atomic geometry of many of these surfaces has now been determined to a relatively high degree of precision [2], and this has allowed calculations of surface core-level shifts to be performed for the first time. For example, a tight-binding approach has recently been used to calculate the surface core-level shift on the (110) surface of a variety of III–V semiconductors [3]. Although, in the majority of cases [4], the agreement between the theoretical predictions and the experimentally determined surface core-level shifts is good, the problem of isolating the major contribution to the surface core-level shift remains. This is because a recent calculation, which was performed using a relatively simple electrostatic model [5], has indicated that the charge transfer between the surface cation and the surface anion sublattices is not significantly different from that in the bulk. This conclusion is at variance with the findings of the predictive, tight-binding treatment of surface core-level shifts [3] and consequently further theoretical work is required to resolve these conflicts and isolate the leading term in the surface core-level shift on the (110) cleavage face.

In this letter, measurements of the shallow In 4d and As 3d core-levels on the InAs(110) surface are presented together with the results of least squares analysis of the core-level lineshapes. The determination of the surface core-level shifts for this surface is important because it means that the surface core-level shifts for the family of semiconductor surfaces that includes GaX(110) and InX(110) where X = P, As and Sb have now been fully determined and consequently it is considerably easier to recognise general trends.
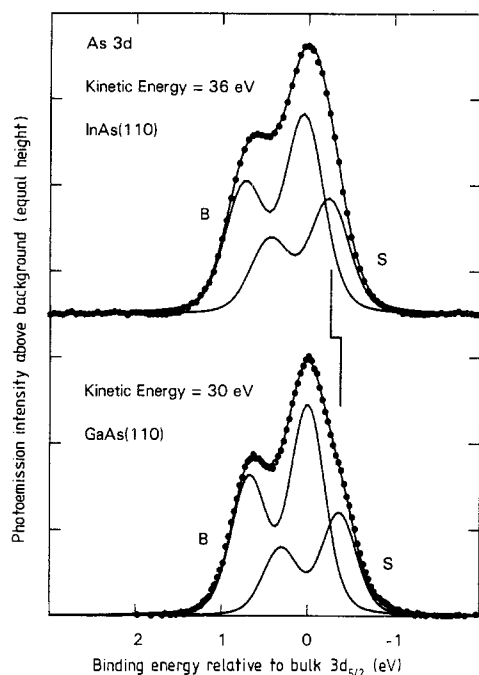
Figure 1. Core-level photoemission from the As 3d core-level on both InAs(110) (upper curve) and GaAs(110) (lower curve). Both spectra were collected under surface-sensitive conditions. The dots represent the experimental points after background subtraction and the line through the points is the sum of the trial functions, which are shown beneath. In both cases the lineshape is well described using two Gaussian broadened, spin–orbit split, Lorentzian doublets, one of which arises from atoms in the bulk and the other of which arises from atoms in the surface layer.
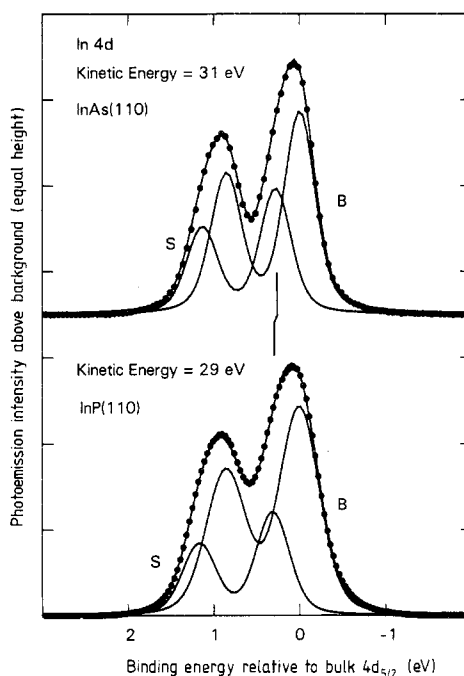
Figure 2. Core-level photoemission from the In 4d core-level on InAs(110) (upper curve) and the In 4d core-level on InP(110) (lower curve) taken under surface-sensitive conditions. Other details are as for figure 1.

The experimental procedure revolved around angle-integrated photoemission experiments performed using an ellipsoidal mirror spectrometer [6] coupled to a 6 m/10 m monochromator [7]. The monochromator was operated in the 6m configuration using a grating that allowed both the In 4d and the As 3d core levels to be examined under both bulk- and surface-sensitive conditions (kinetic energies of $\simeq 10$ eV and $\simeq 35$ eV respectively). The InAs(110) surfaces were prepared by cleaving aligned and prenotched InAs bars, in a preparation chamber adjoining the analysis chamber, at a pressure of $\simeq 2 \times 10^{-10}$ Torr using a blade and anvil. To avoid contamination, the core-level spectra were collected immediately after the bar was cleaved and transferred to the analysis chamber. The surfaces that were examined were 3×3 mm^2 with a very low density of cleavage induced defect steps.

In figure 1, As 3d photoemission spectra from both InAs(110) (upper curve) and GaAs(110) (lower curve) are presented. Both spectra were collected near the escape depth minimum (kinetic energy $\simeq$ 30–35 eV) where the surface-to-bulk intensity ratio is at its maximum. The core-level lineshapes were studied with least squares analysis [8]

Table 1. The full-width half-maximum Lorentzian linewidths (± 0.03 eV), the spin–orbit splitting (± 0.02 eV), the surface-to-bulk core-level binding energy shift (± 0.02 eV) and the spin–orbit branching ratio (± 0.02) determined by least squares optimisation for the In 4d and the As 3d core levels on InAs(110).

	ΔE_L (eV)	ΔE_{SO} (eV)	ΔE_{SB} (eV)	R_{SO}
In 4d	0.152	0.858	+0.28	0.688
As 3d	0.145	0.692	−0.30	0.642

using Voigt trial functions [9]. The parameters that were obtained from the least squares analysis were checked by examining the core-level lineshape at a variety of photon energies in a manner that has been described previously [10]. Figure 1 illustrates that the magnitude of the surface core-level shift on the InAs(110) surface is significantly smaller than the surface core-level shift on the GaAs(110) surface. This affects the total core-level lineshape. On GaAs(110), where the surface core-level shift is larger, the surface core-level produces a well defined shoulder on the low-binding-energy side and the minimum between the bulk As $3d_{5/2}$ and the bulk As $3d_{3/2}$ is deeper.

In figure 2, the In 4d core-level on the InAs(110) surface is compared with the In 4d core-level on the InP(110) surface. Once again, the trial functions are shown beneath the experimental points. In this case the surface core-level shifts are not significantly different, and the main differences in the two spectra arise from the larger instrumental broadening of the In 4d core-level on InP(110). The results of the least squares analysis of the In 4d and the As 3d core-levels on InAs(110) are presented in table 1. The parameters for the In 4d and the P 2p core-levels on InP(110), and the Ga 3d and As 3d core-levels on GaAs(110), have been presented elsewhere [11].

The electron escape depth (Λ) is related to the surface-to-bulk ratio (R_{SB}), and to the interlayer spacing (a_{110}) in the following fashion

$$\Lambda(E) = a_{110}[\ln(1 + R_{SB}(E))]^{-1}$$

where E is the electron kinetic energy. Since the interlayer spacing along the (110) direction is given by $a_0/(2\sqrt{2})$ [2], and the lattice constant of InAs(a_0) is $\simeq 6.06$ Å at room temperature, then $a_{110} \simeq 2.14$ Å. Substituting the surface-to-bulk ratios obtained from the least squares analysis produces escape depths of $\simeq 4.7$ Å (As 3d) and $\simeq 4.5$ Å (In 4d). These values are in good agreement with estimates of the electron escape depth in other III–V semiconductors near the escape depth minimum. For example, the escape depth minimum in both GaAs and InP has been estimated [11] to lie in the range 4.2–5.4 Å. The escape depth minimum in GaP was also found [10] to be $\simeq 5.4$ Å. Notice that since an ellipsoidal mirror analyser was used to collect the core-levels, in the angle integrated mode of operation, the escape depths are averaged over an emission cone of $86°$, which is centred around the sample normal.

A compilation of experimentally determined surface core-level shifts for GaX and InX (X = P, As and Sb) is presented in table 2. In addition, the range of experimentally determined surface core-level shifts have been plotted in figure 3. From the figure it is clear that the surface core-level emission exhibits the same general trend, displaying almost equal and opposite cation and anion surface core-level shifts. The cation surface core-level is shifted to higher binding energy than its parent bulk core-level and the anion surface core-level component is shifted to lower binding energy. Therefore, the

Table 2. Experimentally determined surface core-level binding energy shifts for the cleaved (110) surface of various III–V semiconductors, measured relative to the bulk component. Increases in binding energy are denoted as positive and decreases negative.

	ΔE_A (eV)	ΔE_C (eV)	
GaP(110)	—	+0.28	Eastman *et al* [16, 17]
	−0.41	+0.31	McLean and Ludeke [10]
GaAs(110)	−0.37	+0.28	Eastman *et al* [16, 17]
	−0.38	+0.28	Miller and Chiang [18]
	−0.39	+0.28	Kuhr *et al* [19]
	−0.37	+0.28	McLean [11]
	−0.37	+0.31	Prietsch [20]
GaSb(110)	−0.36	+0.30	Eastman *et al* [16, 17]
InP(110)	—	+0.30	Baier *et al* [15]
	—	+0.30	Kendelewicz *et al* [21]
	−0.31	+0.30	McLean [11]
	−0.31	+0.33	Wilke *et al* [12]
InAs(110)	—	+0.28	Baier *et al* [15]
	−0.30	+0.28	Present study
InSb(110)	−0.29	+0.22	Taniguchi *et al* [13]
	−0.27	+0.24	Hinkel *et al* [14]
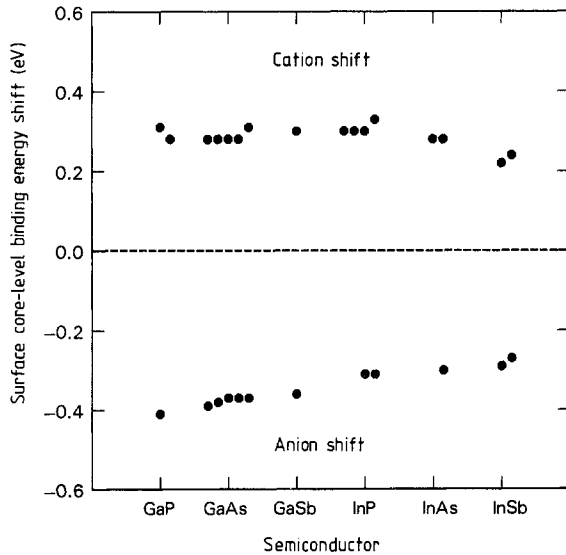
Figure 3. Experimentally determined cation and anion surface core-level shifts, relative to the bulk core-level, for the family of III–V semiconductors GaX and InX where X = P, As and Sb.

binding energy difference between the cation and the anion gets smaller as the surface is approached from the bulk. However, a closer inspection of figure 3 also reveals that the anions exhibits a slightly larger range of surface core-level shifts than the cations. Most of the cation core-level shifts, with the notable exception of InSb(110), lie within the relatively narrow range from +0.28 to +0.33 eV, a difference of only ≈0.05 eV. If
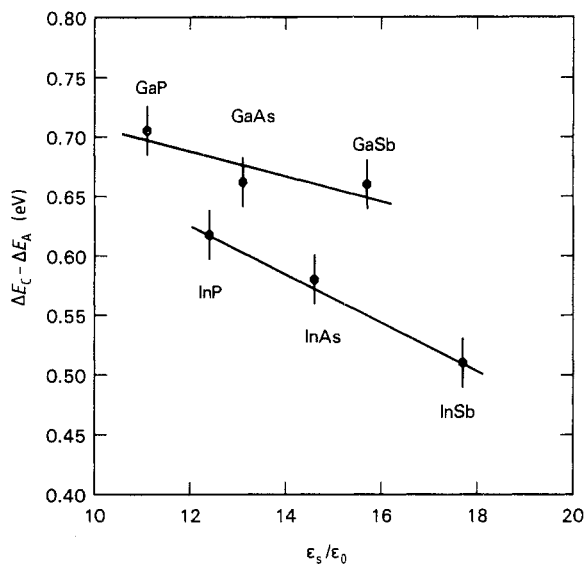
Figure 4. The average surface core-level shift, determined in a manner that is described in the text, $\Delta E_C - \Delta E_A$ (see table 2), is plotted against the relative semiconductor dielectric constant [22]. Lines have been drawn through each of the subgroups (GaP, GaAs, GaSb and InP, InAs, InSb) as a guide to the eye only.

InSb(110) is included, the total difference increases by approximately a factor of 2 (0.11 eV). The largest anion surface core-level shift that has been reported so far is -0.41 eV for the P 2p core-level on GaP(110) [10] and the lowest, for the Sb 4d core-level on InSb(110) [13], is -0.27 eV. This is a difference of $\simeq 0.14$ eV, slightly larger than the corresponding cation difference.

It is also clear that the difference $\Delta E_C - \Delta E_A$, where ΔE_C is the cation surface core-level shift and ΔE_A is the anion surface core-level shift, is generally larger for the more ionic materials, and systematically decreases along the series from GaP to InSb. Most of this change is due to a decrease in the anion surface core-level shift. To illustrate this in more detail, the average core-level shift has been plotted against the semiconductor dielectric constant [22], which is used as a measure of ionicity; see figure 4. This was done by calculating the average anion surface core-level shift for each semiconductor, and subtracting it from the corresponding average cation core-level shift. Basically, this assumes that the estimates of the anion and cation core-level shifts are uncorrelated, which is a reasonable assumption in this instance. This approach has the advantage that all the experimental data points can be used. Plots of the average core-level shift versus either the semiconductor bandgap or the (Pauling) electronegativity difference show the same general trend and grouping. However, the average core-level shift increases with increasing electronegativity difference (i.e. the semiconductor ionicity) and also with increasing semiconductor bandgap, whereas it decreases with increasing dielectric constant. Therefore, although the semiconductor dielectric constant has been used in figure 4, the same trends are displayed by both the electronegativity difference and the semiconductor bandgap. This is not surprising because they are related quantities (see, e.g., [5, 23]). Two lines have been drawn, as guides to the eye, through each of the subgroups (i.e. GaP, GaAs, GaSb and InP, InAs, InSb). It is clear from figure 4 that the average surface core-level shift of each individual subgroup decreases systematically with increasing dielectric constant. Likewise, it increases with increasing electronegativity difference and semiconductor bandgap.

To summarise, the lineshapes of the In 4d and the As 3d core-levels on InAs(110) have been studied using least squares analysis and the surface core-level shifts have been estimated to be $+0.28 \pm 0.02$ and -0.30 ± 0.02 eV respectively. These measurements conclude an investigation of the family of III–V semiconductors which include GaX and InX, where X = P, As and Sb. It has been demonstrated that the surface core-level binding energy difference $(\Delta E_C - \Delta E_A)$ decreases with increasing semiconductor dielectric constant. Similarly, the surface core-level binding energy difference also increases, in a systematic fashion, with increasing electronegativity difference (i.e. ionicity) and with increasing semiconductor bandgap. It has been noted that these parameters are intimately related and that these trends indicate that the size of the surface core-level shift on III–V semiconductors scales with the ionicity of the semiconductor.

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