PHYSICAL REVIEW B VOLUME 39, NUMBER 9 15 MARCH 1989-II

Surface core-level binding-energy shifts for the cleaved GaP(110) surface

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(Received 31 October 1988; revised manuscript received 30 November 1988)

Ga 3*d* and P 2*p* core-level photoemission spectra have been collected from cleaved GaP(110) surfaces and surface core-level binding-energy shifts of −0.41 and +0.31 eV have been obtained for the P 2*p* and Ga 3*d* core levels, respectively. The energy dependence of the P 2*p* core-level line shape has also been studied and estimates of the photoelectron escape depth in GaP are made for photoelectrons with kinetic energies in the range 10–60 eV.

Although the (110) surface core-level binding-energy shifts of several III-V compound semiconductors have already been experimentally determined,[1-5] most of the studies have concentrated on shallow core levels with binding energies of less than 50 eV. However, Kendelewicz *et al.*[5] have recently studied the line shapes of the In 4*d* and the P 2*p* core levels on the InP(110) surface using soft-x-ray photoelectron spectroscopy. They concluded that although the surface core-level binding-energy shift of the cation was +0.30 eV (relative to the bulk core level) the surface core-level binding-energy shift on the P 2*p* core level was immeasurably small. Since all of the (110) surfaces of III-V semiconductors that have been studied so far have anion surface core-level shifts of −0.29 to −0.37 eV (Table I) this result is surprising. However, Priester and co-workers[6] have recently predicted that the surface core-level binding-energy shift on the P 2*p* core level on InP(110) should be exactly equal to zero.

In this paper we have extended the study of surface core-level binding-energy shifts to include the P 2*p* core level on the cleaved GaP(110) surface and demonstrate that the surface core-level shifts are −0.41 and +0.31 eV for the P 2*p* and Ga 3*d* core levels, respectively. These values are in reasonable agreement with the predictions of Priester *et al.*[6] and are also comparable with the surface core-level binding-energy shifts observed on the (110) cleavage face of other III-V semiconductors.[1-5]

The core-level photoemission spectra were collected, in the angle-integrated mode, using an ellipsoidal mirror spectrometer[7] coupled to a 6-m monochromator.[8] The (110) surfaces were prepared by cleaving aligned bars of moderately doped, *n*-type GaP using the wedge-and-anvil technique in ultrahigh vacuum (8×10^{-11} Torr). The quality of the surfaces was ascertained from the core-level spectra themselves; a nonuniform surface potential produces a broadening of the core levels which can be seen under high-resolution conditions, from the intensity of surface features in the valence-band region near the valence-band maximum, and lastly from visual inspection.

TABLE I. Experimentally determined surface core-level binding-energy shifts for the cleaved (110) surface of various III-V semiconductors, measured relative to the bulk component.

	ΔE_A/eV	ΔE_C/eV	
InP(110)	0.00	+0.30	Kendelewicz *et al.*[5]
InSb(110)	−0.29	+0.22	Taniguch *et al.*[3]
InAs(110)		+0.28	Baier *et al.*[15]
GaP(110)		+0.28	Eastman *et al.*[1,2]
	−0.41	+0.31	present study
GaAs(110)	−0.37	+0.28	Eastman *et al.*[1,2]
GaSb(110)	−0.36	+0.30	Eastman *et al.*[1,2]

The line shapes of the P 2*p* and the Ga 3*d* core levels were studied using conventional least-squares analysis.[9] Firstly, the secondary electron background was approximated by a polynomial fitted to the wings of the spectra. Secondly, to reduce the number of parameters to be found by the least-squares routine the Lorentzian linewidths of the bulk and surface components and also the Gaussian linewidths of the bulk and surface components were initially set equal. Subsequently the former condition was relaxed. However, within our experimental accuracy, the approximation that the Gaussian and the Lorentzian linewidths are the same for both the surface and the bulk components is a good one. Thirdly, to further reduce the number of parameters that have to be determined the spin-orbit branching ratio ($R_{\text{s.o.}}$) and the spin-orbit splitting ($\Delta E_{\text{s.o.}}$) are determined independently. This is done by subtracting out one of the spin-orbit components. This procedure has been used successfully on the Si 2*p* core level.[10] Once the branching ratio and the spin-orbit splitting have been determined they are then input into the least-squares fitting procedure as starting parameters.

The least-squares fit was carried out in two stages. An initial fit was carried out on each core level using the starting values for $R_{\text{s.o.}}$ and $\Delta E_{\text{s.o.}}$. This allowed the remaining parameters to be determined approximately. As mentioned previously, the first fits were carried out assuming that the surface and bulk Lorentzian widths are equal and that the Gaussian widths for both surface and bulk are the same. In the final fits all of the parameters were allowed to vary within ±5% of their starting value. The values of the fundamental parameters that we have quoted in Table II are the ones that gave the best fits, with the lowest chi-squared coefficient for the entire range of core-level spectra that we measured.

Since the Ga $3d$ core level has been studied previously, and because the magnitude of the surface core-level binding-energy shift on the P $2p$ has not previously been determined on GaP(110), we will concentrate, in this paper, on the P $2p$ core level. However, in Fig. 1 we present a Ga $3d$ core-level spectrum which was collected using an incident photon energy of 80 eV. The surface core-level binding-energy shift of $+0.31$ eV is similar to the value previously reported by Eastman *et al.*[1] ($+0.28$ eV) but smaller than the theoretical estimate of Priester *et al.*[6] [$+0.41$ eV for the relaxed (110) surface]. The agreement between the results of this study and the results of Eastman *et al.*[1] is encouraging considering that Eastman *et al.*[1] used Lorentzian line shapes and did not incorporate the instrumental Gaussian broadening. The difference between the experimental values and the theoretical estimate may at first appear worrying. However, Priester *et al.*[6] have pointed out that their calculation of the surface core-level shift may be overestimated by up to 0.10 eV.

P $2p$ core-level photoemission spectra are presented in both Figs. 2 and 3. In Fig. 2 the incident photon energy is 170 eV and the photoexcited electrons have a kinetic energy of $\simeq 35$ eV. Under these conditions the photoelectron escape depth is comparatively short (Fig. 4) and the surface-to-bulk ratio attains its maximum value. The P $2p$ core-level photoemission spectrum presented in Fig. 3 was collected near threshold ($E \simeq 10$ eV) and the magnitude of the surface-to-bulk intensity ratio is smaller.

To test whether the parameters describing the core-level photoemission spectra have been determined correctly, we have used the same basic parameters (ΔE_L, ΔE_G, $\Delta E_{\mathrm{s.o.}}$, ΔE_{SB}, $R_{\mathrm{s.o.}}$), constrained to within $\pm 5\%$, to fit all of the P $2p$ core-level photoemission spectra, allowing only R_{SB} to vary by more than $\pm 5\%$. The surface-to-bulk intensity ratio is then estimated for each P $2p$ core-level spectrum and subsequently the photoelectron escape depth can be calculated for electrons with kinetic energy in the range 10–60 eV. Using a discrete layer model[1] results in the following expression for the escape depth:

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

where Λ is the electron escape depth, a_{110} is the interlayer spacing (1.927 Å), and R_{SB} is the surface-to-bulk intensity ratio. The electron escape depth is averaged over the emission cone of 86° centered on the sample normal. The energy dependence of the escape depth is a smoothly varying function resembling the "universal" escape-depth curve (Fig. 4). This procedure serves as a useful double check on the basic parameters that we have obtained from the least-squares analysis.

TABLE II. The values of the Lorentzian linewidth (full width at half maximum), the spin-orbit splitting, the surface-to-bulk core-level binding-energy shift, and the spin-orbit branching ratio determined by least-squares optimization for the P $2p$ and the Ga $3d$ core levels on GaP(110).

	ΔE_L/eV	$\Delta E_{\mathrm{s.o}}$/eV	ΔE_{SB}/eV	$R_{\mathrm{s.o.}}$
P $2p$	0.185	0.876	-0.41	0.540
Ga $3d$	0.170	0.452	$+0.31$	0.655

Our estimates of the escape depth are in agreement with the results of other studies. For example, using the same technique Eastman *et al.*[1] calculated the escape depth in GaAs and GaSb to be 5.9 Å ($E \simeq 40$ eV) and 4.5 Å ($E = 40$ eV), respectively.

Other methods have also been used to determine the electron escape depth. For example, Gant and Mönch[11] have deposited epitaxial Ge overlayers on GaAs(110) and measured the intensities of the Ga, As, and Ge Auger lines. From the attenuation of the bulk Auger lines with increasing overlayer thickness they have estimated the escape depth at various characteristic kinetic energies. They positioned the escape-depth minimum ($\simeq 6$ Å) at $\simeq 55$ eV in GaAs.

Another useful double check on the fundamental parameters is the variation of the Gaussian linewidth. We

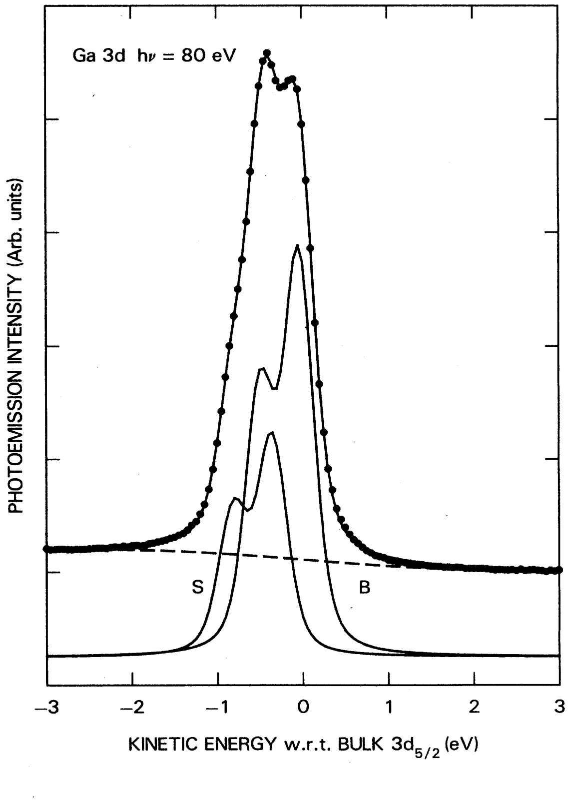

FIG. 1. Ga $3d$ core-level photoemission spectrum excited with 80-eV light ($E \simeq 55$ eV). The raw data is indicated using dots and the solid line is the result of the least-squares fit. The dashed line is the estimated secondary-electron background and the surface (S) and bulk (B) components are shown in the lower portion of the figure. [Kinetic energies are given with respect to (w.r.t.) the bulk levels indicated.]

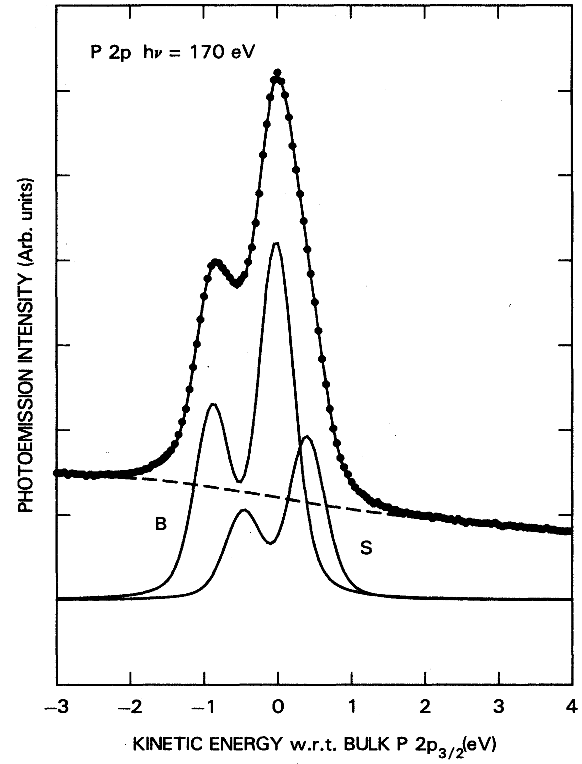

FIG. 2. A P $2p$ core-level photoemission spectrum measured under surface sensitive conditions ($E \simeq 35$ eV) using an incident photon energy of 170 eV near the minimum in the escape-depth curve (see Fig. 4). Other details are as for Fig. 1.

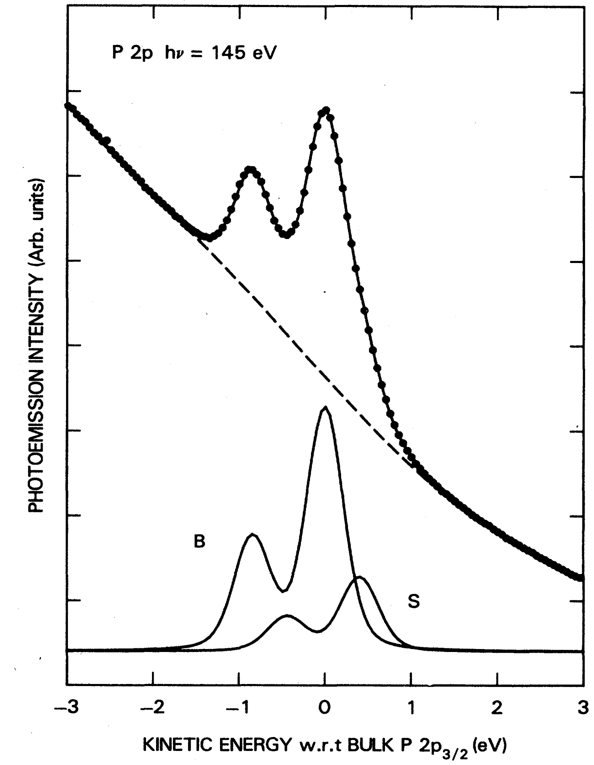

FIG. 3. A P $2p$ core-level photoemission spectrum measured under bulk sensitive conditions ($E \simeq 10$ eV), using an incident photon energy of 145 eV. Other details are as for Fig. 1.

found that the Gaussian linewidth exhibits a linear dependence on photon energy in the range 145–195 eV. We also found the magnitude of the Gaussian broadening (0.4 eV at $h\nu=145$ eV and 0.6 eV at $h\nu=190$ eV) to be significantly larger than the estimated total energy resolution. We attribute this to residual inhomogeneities in the surface potential and cooling the substrate may help to reduce this.

As mentioned earlier, we assumed that the Gaussian linewidths of the surface and bulk components and also the Lorentzian linewidths of the surface and bulk components are equal. However, Kendelewicz *et al.*[5] found for the In $4d$ core level on InP(110) surfaces that the quality of the least-squares fit could be significantly improved by reducing the magnitude of the Lorentzian linewidth of the surface component relative to that of the bulk. We found that, as far as the P $2p$ core level on the GaP(110) surface was concerned, relaxing the condition that the Lorentzian linewidths are the same does not always lead to a lower regression coefficient or a smoother distribution of residuals. Although it is likely that small differences do exist, we found it difficult to determine them reliably using a least-squares optimization procedure.

Turning now to the surface core levels, several attempts have been made to explain the magnitude and po-

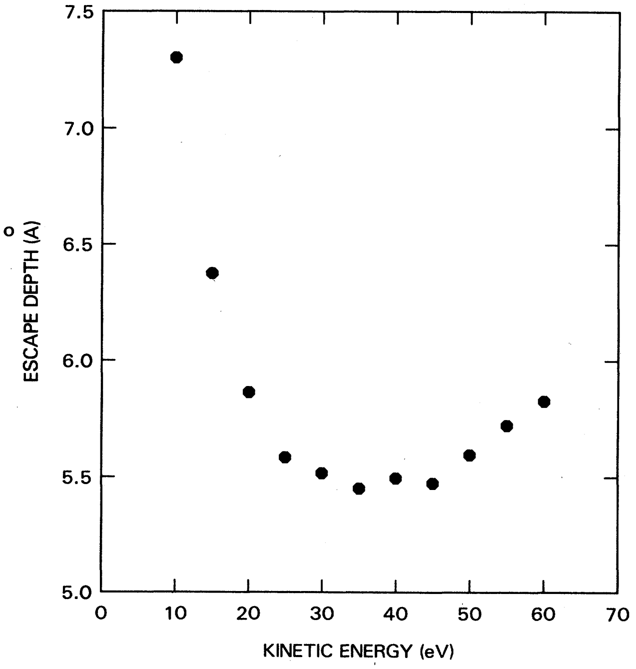

FIG. 4. The photoelectron escape depth $\Lambda(E)$ plotted as a function of the photoelectron's kinetic energy (E).

larity of the surface core-level binding-energy shifts on the (110) cleavage face of III-V semiconductors. Eastman *et al.*[1] originally proposed that the reduced cation-anion binding-energy difference at the surface is a direct consequence of additional surface-charge redistribution. This view has been challenged by Davenport *et al.*[13] and more recently by Mönch.[14] Mönch[14] has argued that the amount of charge transferred from the cations to the anions in the surface layer is the same as that transferred from the cations to the anions in the underlying bulk layers. Consequently, he has concluded that the surface core-level binding-energy shifts are due primarily to the difference between the surface and bulk Madelung potentials.

Moreover, Priester *et al.*[6] have recently calculated the surface core-level binding-energy shift for the (110) cleavage face of several III-V semiconductors. The magnitude of the surface core-level binding-energy shift was calculated utilizing a tight binding approach coupled with a local charge neutrality approximation. They found that the charge redistribution was mainly restricted to the surface layer and that it is reduced by the relaxation of the surface (Fig. 1 of Ref. 6). Bearing in mind that the assumption of local charge neutrality may result in an overestimate of the surface core-level binding-energy shift by up to 0.1 eV, their predictions of the surface core-level shifts on the relaxed GaP(110) surface (-0.43 and $+0.41$ eV for the anion and the cation, respectively) are in reasonable agreement with our experimental values (-0.41 and $+0.31$ eV). They predict that the magnitude of the surface core-level shifts on the GaP(110) surface should be larger than those on the InP(110) surface and that the P $2p$ surface core-level binding-energy shift on InP(110) should be exactly zero.

In light of the above discussion, it is interesting that the core-level photoemission results we have presented in this paper are in marked contrast to those recently presented by Kendelewicz *et al.*[5] for the cleaved InP(110) surface. Kendelewicz *et al.*[5] attempted to fit the P $2p$ core-level line shape using two spin-orbit split doublets but found that the resultant fit has an unphysically small Gaussian linewidth and an inverted surface-to-bulk intensity ratio. The differences between the results of this study and the results of Kendelewicz *et al.*[5] suggest that there are significant physical differences between these two surfaces. However, it is also possible there may be differences in the least-squares fitting routines that have been used. It is interesting to note that Schäffler *et al.*[12] have obtained a fit to the P $2p$ core-level on InP(110), with a physically reasonable bulk-to-surface ratio, under surface sensitive conditions ($h\nu = 180$ eV), with a surface and bulk spin-orbit split doublet. In addition, Hinkel *et al.*[4] have recently quoted a value of -0.24 eV for the P $2p$ surface core-level shift on InP(110). Therefore, the conclusion that we alluded to earlier, that there are significant differences between the InP(110) and GaP(110) surfaces, is not completely watertight and another study of the P $2p$ core-level emission on the InP(110) surface may help to clarify the differences that we have noted here.

To conclude, the line shapes of the Ga $3d$ and the P $2p$ core levels on the GaP(110) surface have been studied with soft-x-ray photoemission spectroscopy. Using conventional least-squares analysis the basic parameters describing the core-level photoemission have been estimated. The surface core-level binding-energy shifts for the Ga $3d$ and the P $2p$ core levels are $+0.31$ and -0.41 eV, respectively. The Ga $3d$ core-level shift is in good agreement with the previous estimate of Eastman *et al.*[1] ($+0.28$ eV). The values that we have obtained for both the anion and the cation surface core-level binding-energy shifts are in reasonable agreement with the recent theoretical prediction of Priester *et al.*[6] taking into account that their estimates of $+0.41$ and -0.43 eV for the cation and anion shifts, respectively, may be overestimated by up to 0.10 eV.

We would like to acknowledge discussions with F. J. Himpsel and the assistance of M. Prikas, J. Yurkas, A. Marx, and C. Costas. Research was carried out in part at the Brookhaven National Laboratory, which is sponsored by the U.S. Department of Energy (Division of Materials Science and Division of Chemical Sciences).

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