

Commutativity of the GaAs/AlAs (100) band offset

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X-ray photoelectron spectroscopy is used to measure the valence-band offset *in situ* for GaAs/AlAs (100) heterojunctions grown by molecular beam epitaxy. Ga 3*d* and Al 2*p* core level to valence-band edge binding energy differences are measured in GaAs (100) and AlAs (100) samples, respectively, and the Al 2*p* to Ga 3*d* core level binding energy difference is measured in GaAs–AlAs (100) and AlAs–GaAs (100) heterojunctions. Measurements of the Al 2*p* to Ga 3*d* core level energy separations indicate that the band offset for GaAs/AlAs (100) is commutative; the value we obtain is $\Delta E_v = 0.46 \pm 0.07$ eV. Our observation of commutativity is believed to be a consequence of the high quality of our GaAs/AlAs (100) heterojunctions, and of the inherent commutativity of the GaAs/AlAs (100) band offset.

I. INTRODUCTION

Band offsets at semiconductor heterojunctions are of great importance in solid-state physics, both from a fundamental point of view and for device applications. The GaAs/AlAs band offset in particular has been a subject of extensive study, due to the technological importance of the GaAs/Al_xGa_{1-x}As heterojunction system. An important but unresolved experimental issue in this system is that of commutativity (i.e., independence of growth sequence) of the band offset. Commutativity is consistent with current theoretical models and some experimental results^{1,2}; however, a dependence of the band offset on growth sequence has also been reported.^{3,4} Published experimental values^{1,4-8} for the GaAs/AlAs valence-band offset range from $\Delta E_v = 0.36$ eV to $\Delta E_v = 0.56$ eV.

In this paper we present the results of measurements of the band offset in GaAs–AlAs (100) and AlAs–GaAs (100) heterojunctions using x-ray photoelectron spectroscopy (XPS); we adopt the convention of listing the top layer in the heterojunction first, e.g., GaAs–AlAs indicates a heterojunction with GaAs grown on top of AlAs; GaAs/AlAs refers collectively to both growth sequences. We describe sample preparation and experimental techniques in Sec. II. In Sec. III we present and discuss the results of our experiments. Sec. IV concludes the paper.

II. EXPERIMENT

The samples studied in this experiment were grown by molecular beam epitaxy (MBE) in a PHI 430 growth chamber on Si-doped *n*⁺-GaAs (100) substrates. The substrate preparation consisted of a degrease followed by a 90-s etch in 5:1:1 H₂SO₄:H₂O₂:H₂O. The native oxide was desorbed in the growth chamber by heating the substrate to ~610 °C in an As flux. All of the samples were grown at 600 °C and were lightly doped *n*-type with Si ($n \approx 1 \times 10^{16}$ cm⁻³) to avoid both sample charging effects and excessive band bending due to Fermi-level pinning at the surface of the specimen.

Epitaxial GaAs layers > 1 μm in thickness were used to make the bulk GaAs XPS measurements. Electron mobilities in these films were comparable to those typically report-

ed for high-quality MBE growth,⁹ and the samples exhibited good photoluminescence at low temperatures. Two bulk AlAs samples were grown for this study; each consisted of a 2500-Å-thick epitaxial AlAs layer, with one grown on top of a 1.5-μm GaAs buffer layer and the other on top of a 1500-Å Al_{0.3}Ga_{0.7}As buffer.

Two types of heterojunction samples were grown, allowing the commutativity of the band offset to be checked. One type consisted of 25 Å of GaAs on top of either 500, 200, or 100 Å of AlAs, while the other consisted of 25 Å of AlAs on top of 1000 Å of GaAs; growth interruption was not used in fabricating the heterojunction samples. In both cases, the interfaces were believed to be fairly abrupt based upon results from quantum well photoluminescence (the quantum well luminescence peak width was 3.8 meV full width at half-maximum (FWHM) at 9 μW/cm² incident power) and double-barrier resonant tunneling experiments on samples with similarly grown interfaces.

XPS measurements were obtained using a Perkin-Elmer Model 5100 analysis system; samples were probed using a monochromatized Al Kα x-ray source ($h\nu = 1486.6$ eV), and electron energies were measured by a spherical capacitor analyzer. Au 4*f* core level peaks had full widths at half-maximum of ~0.73 eV. The base pressure in the XPS chamber is typically $\sim 5 \times 10^{-10}$ Torr, and the analysis chamber is connected to the MBE chamber via a UHV transfer tube, allowing samples to be grown and analyzed without being exposed to atmosphere. This arrangement eliminates experimental uncertainties associated with surface passivation, sputter cleaning, and annealing of samples that have been transferred through atmosphere. Measurements were obtained from three pure GaAs (100) and two pure AlAs (100) samples, and from three GaAs–AlAs (100) and two AlAs–GaAs (100) heterojunctions. Figure 1 shows a schematic energy-band diagram for the GaAs/AlAs interface. The core levels of interest in the band offset measurement are the Al 2*p* level and the Ga 3*d* level in AlAs and GaAs, respectively. From Figure 1, it can be seen that the valence-band offset is given by

$$\Delta E_v = (E_{\text{Al } 2p}^{\text{AlAs}} - E_{\text{Ga } 3d}^{\text{GaAs}}) + (E_{\text{Ga } 3d}^{\text{GaAs}} - E_v^{\text{GaAs}}) - (E_{\text{Al } 2p}^{\text{AlAs}} - E_v^{\text{AlAs}}). \quad (1)$$

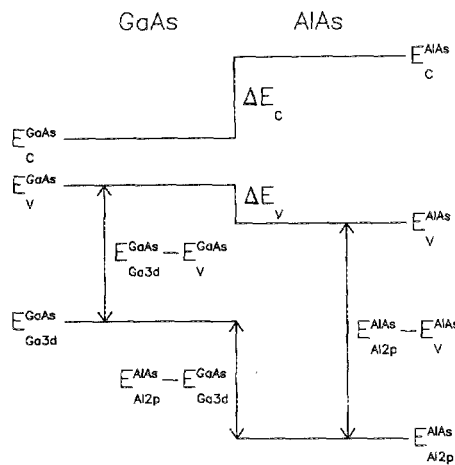


FIG. 1. Schematic energy band diagram for the GaAs/AlAs interface.

The core level to valence-band edge binding energy differences are obtained from measurements on pure GaAs and AlAs samples, and the Al 2*p* to Ga 3*d* core level binding energy differences are obtained from the heterojunction samples.

For each sample, a binding energy window that included all energy levels of interest was scanned repeatedly for ~15–20 h. Due to the low count rate for electrons near the valence-band edge, energies in that region were sampled for a longer time than energies in other parts of the spectrum. Spectra from pure GaAs and pure AlAs and from GaAs–

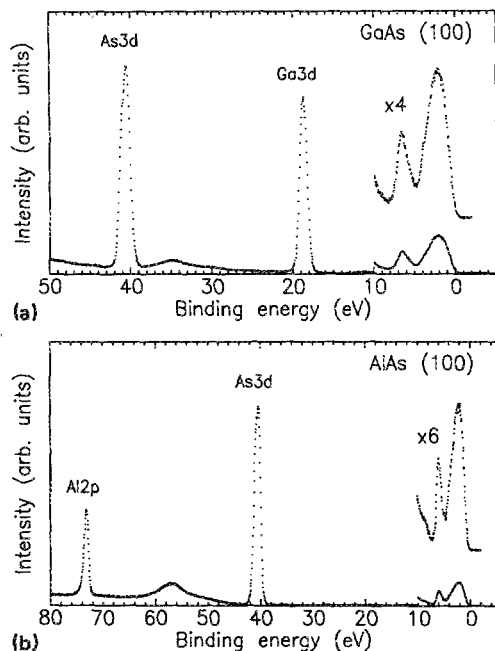


FIG. 2. Representative binding energy XPS spectra for (a) GaAs (100) and (b) AlAs (100) samples. Core level to valence-band edge binding energy differences are obtained from these spectra. The discontinuities in the spectra at 10 eV binding energy are due to the longer sampling times used during data acquisition near the valence-band edge; the valence-band spectra are also shown on enlarged intensity scales, as indicated in the figure.

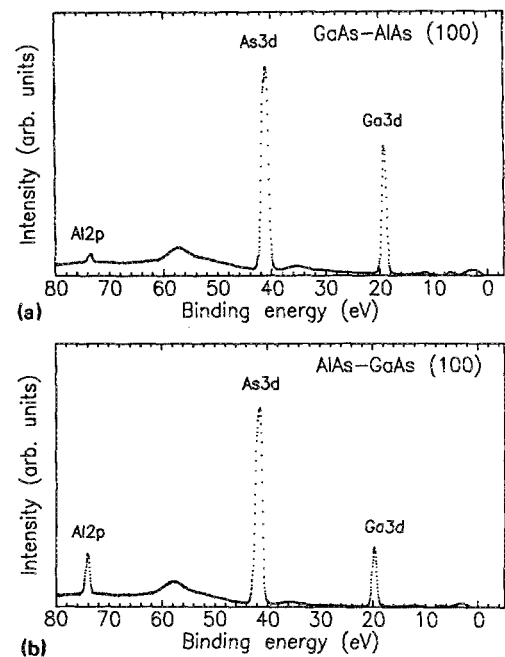


FIG. 3. Representative binding energy XPS spectra for (a) GaAs–AlAs (100) and (b) AlAs–GaAs (100) heterojunction samples. Core level to core level binding energy differences are obtained from these spectra.

AlAs and AlAs–GaAs heterojunctions are shown in Figs. 2 and 3, respectively. In Fig. 2, the discontinuities in the spectra at 10-eV binding energy are due to the longer sampling time near the valence-band edge; the valence-band spectra are also shown on enlarged scales, as indicated in the figure.

To obtain accurate core level to core level and core level to valence-band edge binding energy differences, it is necessary to determine peak positions and valence-band edge positions to a high degree of precision. To find core level peak positions, we subtracted from each core level peak a background (arising from inelastic scattering in the sample) proportional to the integrated photoelectron intensity, and defined the peak energy to be the midpoint of the two energies at which the intensity was one-half the maximum intensity. The uncertainty in this determination of the peak position was taken to be ± 0.02 eV, and typically core level energy separations were reproducible to better than ± 0.01 eV for a given sample.

To locate the position of the valence-band edge in the XPS spectrum, we employed the precision analysis technique developed by Kraut *et al.*¹⁰ In this approach, the XPS spectrum near the valence-band edge is modeled as a convolution of a theoretical valence-band density of states with an experimentally determined XPS instrumental resolution function. This model function is then fitted to the experimental data to give the position of the valence-band edge. Due to the similarity in the valence-band spectra for GaAs and AlAs,⁴ we were able to use the GaAs nonlocal pseudopotential valence-band density of states¹¹ in analyzing data from both materials. For a given sample, core level to valence-band edge binding energy differences were reproducible to better than ± 0.04 eV.

When determining the position of a valence-band edge

using this method, complications can arise from the presence of surface states in the same energy region as the valence band.¹⁰ These surface states produce contributions to the XPS spectrum that are unaccounted for in the theoretical valence-band density of states, and can affect the calculated position of the valence-band edge by ~ 0.1 eV or more. No such effects were observed in our AlAs (100) samples, but a p_z -like surface state was detected in the GaAs (100) samples, in agreement with previous studies of the GaAs (100)-(2 \times 4) reconstructed surface.¹² Thus, the position of the GaAs valence-band edge was determined by analyzing the XPS valence-band spectrum only in an energy region in which no surface states were observed.

III. RESULTS AND DISCUSSION

The measured core level to valence-band edge binding energy differences are shown in Table I. For GaAs (100), the result in $(E_{\text{Ga}3d}^{\text{GaAs}} - E_v^{\text{GaAs}}) = 18.73 \pm 0.05$ eV, and for AlAs (100) we obtain $(E_{\text{Al}2p}^{\text{AlAs}} - E_v^{\text{AlAs}}) = 72.71 \pm 0.04$ eV. These values are in good agreement with those obtained by Waldrop, Grant, and Kraut.⁴ Table II lists the core level binding energy differences for the AlAs-GaAs (100) and GaAs-AlAs (100) heterojunctions. For the GaAs-AlAs interface, we find $(E_{\text{Al}2p}^{\text{AlAs}} - E_{\text{Ga}3d}^{\text{GaAs}}) = 54.45 \pm 0.02$ eV. Using Eq. (1), we see that this value corresponds to a valence-band offset of 0.47 ± 0.07 eV. The core level binding energy difference for the AlAs-GaAs (100) interface was found to be $(E_{\text{Al}2p}^{\text{AlAs}} - E_{\text{Ga}3d}^{\text{GaAs}}) = 54.43 \pm 0.02$ eV, corresponding to a valence-band offset of 0.45 ± 0.07 eV.

From these measurements we see that the valence-band offsets for the two different growth sequences are within 0.02 eV of each other, indicating that the GaAs/AlAs (100) band offset is commutative. The observation of commutativity for GaAs/AlAs (100) is in agreement with the result of Katnani and Bauer,¹ but disagrees with that of Waldrop *et al.*,⁴ who reported a dependence of the band offset on both growth sequence and crystal orientation. The fact that XPS band offset measurements are not consistently commutative or noncommutative would seem to indicate that growth conditions and interface quality can have a significant effect on the value of the band offset. If this were the case, one would expect that nearly ideal interfaces would exhibit commutativity, while nonideal interfaces would not.

The value obtained for the band offset, 0.46 eV, is well within the range of experimental values that have been reported. XPS measurements by Waldrop *et al.*⁴ yielded a valence-band offset of 0.46 eV for the AlAs-GaAs (100) heter-

TABLE I. Measured core level to valence-band edge binding energy differences for GaAs (100) and AlAs (100).

Semiconductor	Sample	$E_{\text{Ga}3d}^{\text{GaAs}} - E_v^{\text{GaAs}}$ (eV)	$E_{\text{Al}2p}^{\text{AlAs}} - E_v^{\text{AlAs}}$ (eV)
GaAs (100)	III024	18.75	
GaAs (100)	III031	18.72	
GaAs (100)	III054	18.73	
AlAs (100)	III027		72.70
AlAs (100)	III058		72.72

TABLE II. Measured Al2p to Ga 3d core level binding energy differences for GaAs-AlAs (100) and AlAs-GaAs (100) heterojunctions.

Heterojunction	Sample	$E_{\text{Al}2p}^{\text{AlAs}} - E_{\text{Ga}3d}^{\text{GaAs}}$ (eV)
GaAs-AlAs (100)	III036	54.44
GaAs-AlAs (100)	III085	54.46
GaAs-AlAs (100)	III087	54.45
AlAs-GaAs (100)	III045	54.43
AlAs-GaAs (100)	III050	54.42

ojunction, in agreement with our result, but gave a value of 0.36 eV for the GaAs-AlAs (100) band offset. The latter result suggests that, for the GaAs-AlAs (100) system, differences in growth conditions between our samples and those of Waldrop *et al.* significantly influenced the quality of the interface.

Our measurement of the valence-band offset also gives results comparable to those obtained in electrical measurements. Using the charge transfer technique, Wang and Stern⁷ obtained a valence-band offset of 0.45 ± 0.05 eV, in excellent agreement with our results. Batey and Wright⁵ measured a valence-band offset of 0.55 eV by measuring the activation energy for thermionic emission of holes over an AlAs barrier; this value is somewhat higher than ours, but still approximately within the range of experimental error.

IV. CONCLUSIONS

We have measured the valence-band offset at the GaAs/AlAs (100) interface using XPS. Our measurements indicate that the band offset is commutative, and the value we obtain is $\Delta E_v = 0.46 \pm 0.07$ eV. This value is in good agreement with other XPS band offset measurements, as well as with electrical determinations of the GaAs/AlAs (100) valence-band offset. Our observation of commutativity is in agreement with some, but not all, published results for the GaAs/AlAs (100) interface. This indicates that we have been able to grow high-quality interfaces between GaAs and AlAs, since we expect commutativity in ideal interfaces, and suggests that commutativity of the band offset may safely be assumed in analyzing and designing quantum structures and devices.

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