PHYSICAL REVIEW B VOLUME 33, NUMBER 2 15 JANUARY 1986

Commutativity and transitivity of GaAs-AlAs-Ge(100) band offsets

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(Received 8 August 1985)

X-ray photoemission spectroscopy is used to measure the valence-band offset ΔE_v for *in situ* molecular-beam-epitaxy—grown heterojunctions involving AlAs, GaAs, and Ge. Commutativity is found by the equivalence of the Al($2p$)-Ga($3d$) energy separation (54.65 ± 0.05 eV) for the AlAs-GaAs(100) junction independent of the growth sequence. Transitivity is satisfied by the zero (0.05 ± 0.15 eV) sum of the core-energy separations for AlAs/Ge, GaAs/AlAs, and GaAs/Ge junctions. The band offsets for GaAs-AlAs are more evenly divided between valence and conduction band than the conventional 15—85 % distribution, respectively.

I. INTRODUCTION

Technological application of semiconductor-semiconductor interfaces depends on the potential step across the heterojunction satisfying certain basic relationships.[1-3] Band offsets for a given pair of semiconductors must be equivalent independent of the order of growth. Such a *commutativity* property has been considerably controversial,[4-7] especially for AlAs-GaAs(110) heterojunctions.[4] Further, combinations of different junctions should combine in a predictable fashion if the sum of any two heterojunctions having one semiconductor in common is to yield the value for the third combination. This *transitivity* property will be satisfied if the interface influence on the band offset is negligible compared to the intrinsic, bulk contribution. While both theoretical[8,9] models and some experimental[5,10,11] evidence support the basically bulk nature of the physics responsible for the band offsets, transitivity has not been measured for some of the most important model systems such as AlAs-GaAs-Ge. Extensive studies of a large ensemble of different heterojunctions showed that bulk property theories predict the band offset within 0.2 eV.[5] Also, extensive studies of the GaAs/Ge interfaces have demonstrated the insensitivity of the band offset to interfacial contributions within ±0.05 eV.[10,11] While this establishes characteristics of individual heterojunctions, a single set of experiments is necessary to establish a consistent set of data by which to test band offsets relationships.

In this paper, we present experimental evidence in favor of both the commutativity and transitivity of the band offsets. The results are obtained from x-ray photoelectron spectroscopy (XPS) measurements of the band offset for three heterojunctions involving AlAs, GaAs, and Ge. Our results show that the band offset is commutative within ±0.1 eV and transitive within ±0.15 eV, the limits of our experiment. Further, our results provide the first XPS measurement of the band offset for the technologically important AlAs/GaAs(100) heterojunction. Earlier XPS measurements have been performed only on the AlAs/GaAs(110) heterojunction.[4] An accurate estimate of the band offset greatly relies on the accuracy of the core binding energies. Using available data, the measured valence-band offset is 0.39 ± 0.07 eV for the AlAs/GaAs(100) heterojunction independent of the growth sequence, and it is 0.78 ± 0.07 eV for the AlAs/Ge(100) heterojunction.

II. EXPERIMENT

Si-doped GaAs(100) substrates (5×5 mm^2) were chemopolished and etched in a $5H_2SO_4{:}1H_2O_2{:}1H_2O$ solution. The sample then was mounted on a Moly holder with In contact. The sample was introduced to the main chamber via an interlock. The pressure inside the main chamber is maintained in the $1-2\times10^{-10}$ Torr range. Ar ions with 1 keV energy were used to sputter clean the GaAs surface. The sample then was characterized by Auger-electron spectroscopy and, if no residual contaminations were found, annealed at 550 °C. The annealed surface exhibited a 1×1 or a weak 4×6 low-electron energy diffraction pattern. A buffer layer of GaAs of 1000 Å thick was grown by molecular-beam epitaxy (MBE). The growth parameters are described elsewhere.[10] Twenty-five Å of AlAs then were epitaxially grown on the As-rich GaAs surface [$c(4\times4)$] at the rate of 2 Å/min as determined from the deposition rate of Al. To study the AlAs/GaAs system, 25 Å of GaAs were epitaxially grown on a thick layer of AlAs (500 Å).

The clean surfaces and interfaces were probed with Al $K\alpha$ (1486.6 eV) photons provided by a homemade x-ray lamp. The emitted photoelectrons were collected with a standard Physical Electronics PHI double-pass cylindrical mirror analyzer. The overall experimental resolution was 0.85 eV as obtained from the reported Al $K\alpha$ linewidth.

Measurements were obtained from three (two) freshly MBE-grown GaAs-AlAs (AlAs-GaAs) systems. The results of the different measurements were all consistent within ±0.05 eV. We take this as our experimental uncertainty.

III. RESULTS AND DISCUSSION

Figure 1 shows the energy-band diagram near the interface region for a general heterojunction. The valence-band offset is given by

$$\Delta E_v^{1-2} = \Delta E_b^{c1-c2} + E_b^{c2} - E_b^{c1} , \qquad (1)$$

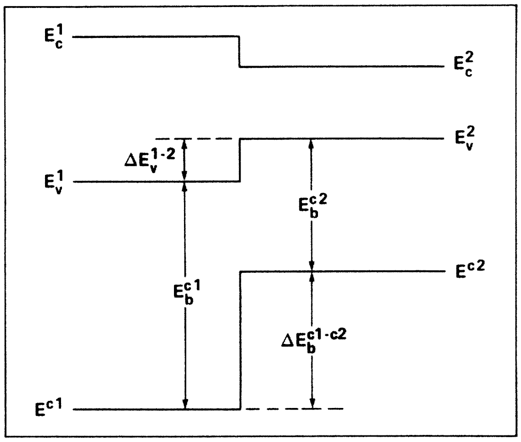

FIG. 1. Schematic of the energy-band diagram near the interface is shown for a general heterojunction. The core-energy separation which is directly obtained from our measurements is related to the band offsets.

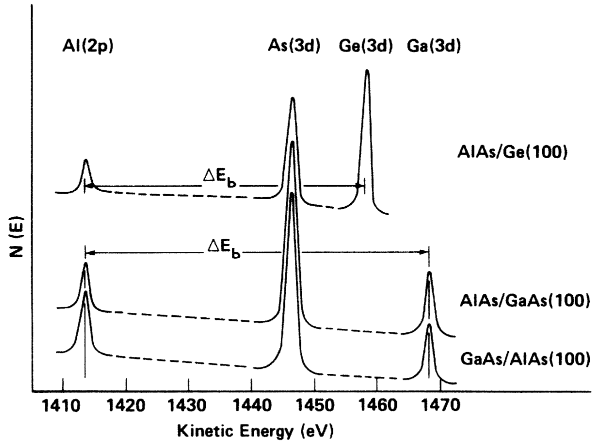

FIG. 2. Energy distribution curves of the As(3*d*), Ga(3*d*), Ge(3*d*), and Al(2*p*) taken with 1486.6 eV photon energy from 25 Å of Ge on AlAs (upper curve), 25 Å of AlAs on GaAs (middle curve), and 25Å of GaAs on AlAs (lower curve).

where E_b^{c1} and E_b^{c2} are the binding energies of the cores relative to the top of the valence band, and ΔE_b^{c1-c2} is the energy separation between the cores. Both E_b^{c1} and E_b^{c2} are constant numbers for the semiconductors under study. Therefore, ΔE_v^{1-2} can be expressed as

$$\Delta E_v^{1-2} = \Delta E_b^{c1-c2} + \text{constant} \ . \qquad (2)$$

Hence, an absolute measurement of the band offset requires precise measurements of the constant in Eq. (2). However, to test both the band offset transitivity and commutativity, one needs only to measure ΔE_b^{c1-c2}, as we will discuss later.

Figure 2 shows photoemission spectra of the Al(2*p*), As(3*d*), Ga(3*d*), and Ge(3*d*) for the AlAs/GaAs (100), GaAs/AlAs(100), and AlAs/Ge(100) heterojunction systems. The energy separation between the Al(2*p*) and Ga(3*d*) for the different experimental runs is listed in Table I. Also shown in the table are the energy separations between the Al(2*p*) and Ge(3*d*) for the AlAs/Ge(100) heterojunction and between the Ga(3*d*) and Ge(3*d*) for the GaAs/Ge(100) heterojunction. The core peak position is determined from the center of gravity of the core line shape, i.e., the center of the full width at half maximum.

A. Band offset commutativity

Commutativity is satisfied when

$$\Delta E_v^{1-2} = \Delta E_v^{2-1} \ . \qquad (3)$$

Using Eq. (2), we find that the commutativity can be directly tested by comparing the measured core-energy separation ΔE_b^{c1-c2} upon changing the growth sequence. As seen in Table I, the average energy separation between Al(2*p*) and Ga(3*d*) is 54.65±0.05 eV for *both* the AlAs/GaAs(100) and the GaAs/AlAs(100) heterojunctions. Contrary to earlier XPS measurements[4] performed on the GaAs/AlAs(110) heterojunction, our result demonstrates that the band offset for the technologically important heterojunction, GaAs/AlAs(100), is commutative. This independence on the growth sequence is consistent with experimental observations from quantum well structures involving these two semiconductors. In addition, the reported core-energy separation for the

TABLE I. Measured core-energy separations ΔE_b for the heterojunctions studied here. ΔE_b can be used directly to test both band offset commutativity and transitivity. To obtain an absolute value for the valence band offset ΔE_v we took published core binding energies for the Al(2*p*), Ga(3*d*), and Ge(3*d*) as 73.1, 18.83, and 29.57 eV, respectively.

Heterojunction		ΔE_b (eV)		ΔE_v (eV)
AlAs/GaAs(100)		54.62		
			54.65	0.38
		54.67		
	Al(2*p*)-Ga(3*d*)			
		54.60		
GaAs/AlAs(100)		54.70	54.66	0.39
		54.66		
AlAs/Ge(100)	Al(2*p*)-Ge(3*d*)		44.31	0.78
GaAs/Ge(100)	Ge(3*d*)-Ga(3*d*)		10.30	0.44

GaAs/AlAs(110) heterojunction is 54.5 and 54.25 eV depending on the growth sequence which is lower than our measured value for GaAs/AlAs(100).

The observed commutativity of the band offset is not only of technological importance, it is also of scientific importance. The band offset commutativity is implicitly assumed in models used to interpret transport and optical measurement performed on III-V/III-V heterojunction structure. Our result is the first experimental support of such assumption. Most of the experimental data available to test the band offset commutativity come from III-V/IV heterojunction systems.[6,7] A number of problems arise when a III-V semiconductor is grown on a group IV semiconductor. Kroemer has discussed these problems and suggested methods to avoid them.[12] Therefore, it is necessary to separate the effect of such problems from real noncommutativity effects. Heterojunctions formed between elemental semiconductors such as Si and Ge are found to support the band offset commutativity.[5] The only XPS data on III-V/III-V heterojunction systems come from the AlAs/GaAs(110) interface which show noncommutativity. Our observation provides the first XPS experimental evidence in favor of the band offset for the III-V/III-V heterojunction system AlAs/GaAs(100) being independent of growth sequence.

B. Band offset transitivity

Transitivity is satisfied when

$$\Delta E_v^{1-2}+\Delta E_v^{2-3}+\Delta E_v^{3-1}=0 . \tag{4}$$

Using Eq. (1), we find that transitivity is satisfied if

$$\Delta E_b^{c1-c2}+\Delta E_b^{c2-c3}+\Delta E_b^{c3-c1}=0 . \tag{5}$$

Table I shows the energy separation between the Al($2p$) and Ga($3d$), and Ge($3d$) as obtained for the AlAs/Ge(100) and GaAs/Ge(100) heterojunctions, respectively. Notice that the sum of the second column in Table I is 0.05±0.15 eV; i.e., the sum of core-energy separations for the AlAs/Ge, GaAs/Ge, and AlAs/GaAs is equal to 0.05±0.15. This sum is practically zero within the experimental uncertainty. This observation supports the transitivity of the band offset. Earlier XPS measurements by Grant *et al.* have shown band offset nontransitivity of 0.64 eV for the CuBr-Ge-GaAs.[13] However, recently Katnani and Margaritondo have tested the transitivity property for a large ensemble of heterojunction systems. They found that band offset transitivity is satisfied on the average within ±0.15 eV.[5] Here, we provide the first experimental evidence in favor of the band offsets commutativity and transitivity in a lattice matched heterojunction system.

Both observations, the commutativity and transitivity of the band offset, demonstrate the insensitivity of the band-structure lineup to interfacial dipoles within ±0.1 eV. This is consistent with recent theoretical studies by Zur *et al.*,[14] and experimental ones by Katnani *et al.*[10,11] Our observations suggest that theoretical models based simply on bulk semiconductor properties should provide a good explanation for the origin of band discontinuities.

C. AlAs/GaAs(100) and AlAs/Ge(100) band offsets

The band offset relationships above were obtained strictly from the measured data. While these relative measures of offsets can be analyzed self-consistently, our results can also be used directly to estimate the band offset for AlAs/GaAs(100) and AlAs/Ge(100) heterojunctions. A precise estimate of the band offset requires knowledge of the binding energies of the core level involved relative to their respective valence band maximum [see Eq. (1)]. The binding energies of Ga($3d$) and Ge($3d$) are 18.83±0.03 and 29.57±0.03 eV, respectively, as reported by Kraut *et al.*[15,16] A precise value for the binding energy of Al($2p$) is lacking in the literature. Therefore, our value of the band offset for the AlAs/GaAs and AlAs/Ge systems relies heavily on what value we use for the Al($2p$) binding energy in AlAs. To our best knowledge, the best value available is 73.1 eV,[17,18] which we use to estimate the band offsets. The last column in Table I shows the band offset obtained using core-level binding energies cited in Refs. 16 and 19 for the three heterojunctions studied here.

Considering these values, we measure 0.38 eV for the band offset for the GaAs/AlAs(100) heterojunction independent of the growth sequence and 0.78 eV for the band offset for the AlAs/Ge(100) heterojunction as listed in Table I. Our value for the AlAs/GaAs heterojunction system agrees well with a recently published value by Tersoff.[20] If we take 2.16 eV as the indirect energy-band gap for AlAs and 1.43 eV as the energy-band gap for GaAs, we find that the valence band offset is $0.5\Delta E_g$, contrary to the widely used Dingle rule, $0.15\Delta E_g$.[21] The current values for the valence-band offset ranges from $0.3-0.5\Delta E_g$ as estimated from photoluminescence and C-V data.[22,23] These first XPS measurements of the AlAs-GaAs system thus support a more equal distribution of offsets between valence and conduction band discontinuities than Dingle originally reported.[21]

While transitivity and commutativity for GaAs-AlAs-Ge(100) support bulk-related theories for band offsets, all such models to date have a common feature of being based on valence state properties. Then for the heterojunction system in question, which consists of a common anion (e.g., As in GaAs/AlAs), one expects a very small valence-band discontinuity compared to the conduction band discontinuity. Indeed the models of Harrison,[9] Frensly-Kroemer,[8] and McCaldin, *et al.*,[24] all predict ΔE_v much smaller than ΔE_c for the AlAs/GaAs system. A recent theory by Tersoff based on energy-band tailing to offset interface dipoles has predicted a band discontinuity which agrees with our measured value for the AlAs/GaAs heterojunction system. However, it remains an outstanding problem to find an explanation for these band offsets based on bulk semiconductor properties which yield nearly equal valence and conduction discontinuities as we measure for the AlAs-GaAs(100) heterojunction system.

ACKNOWLEDGMENTS

This work is supported by the U.S. Office of Naval Research (through L. R. Cooper) under Contracts No. N00014-81-C-0696 and No. N00014-82-C-0338. We would like to thank J. Waldrop, R. Ludeke, and R. Bachrach for providing the necessary core binding-energy data to estimate the band offsets.

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