Microscopic Capacitors and Neutral Interfaces in III-V/IV/III-V Semiconductor Heterostructures

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We examined band discontinuities in AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) single-quantum-well structures, as well as individual isolated Ge-GaAs(001), Ge-AlAs(001), GaAs-Ge(001), and AlAs-Ge(001) heterojunctions. We found that well-defined inequivalent neutral interfaces are established in III-V/IV/III-V structures for Ge coverages as low as 1–2 monolayers. Deviations from the transitivity and commutativity rules of heterojunction behavior reflect inequivalent local interface environments rather than charged interfaces.

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Investigations of the effect of thin Si and Ge interlayers in AlAs-GaAs heterojunctions [1] as well as III-V intralayers in IV/IV homojunctions [2] have detected large changes in the band discontinuities. Such experiments have been motivated by an attempt to exploit the charged character of ideally abrupt polar interfaces between heterovalent semiconductors [3–7] to synthesize a microscopic capacitor [8] on an atomic scale. At variance with such a picture, we show here that *neutral* interfaces are present in III-V/Ge/III-V structures at least for Ge layer thicknesses above 1–2 monolayers. The lack of transitivity and commutativity of the band discontinuities is explained by differences in the local atomic arrangement which lead to *inequivalent* neutral III-V/Ge and Ge/III-V interfaces.

We examined AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) structures for Ge layer thicknesses of 2, 4, 8, 14, and 16 monolayers (ML), as well as isolated Ge/III-V and III-V/Ge interfaces. All structures were grown on GaAs(001) substrates by molecular-beam epitaxy (MBE) in a multichamber facility that includes a monochromatic x-ray photoemission (XPS) spectrometer. XPS was used to determine the valence-band offsets ΔE_v at the different interfaces [9,10] as well as to monitor growth and interdiffusion [11]. Growth of GaAs(001)2 $\times$4 and AlAs(001)3$\times$1 substrates was performed following the methodology described in Ref. [1]. Pseudomorphic n^+-Ge layers were grown at 360 °C at a rate of 300 Å/h under an As partial pressure of 2×10^{-8} Torr, and exhibited a 2$\times$2 reconstruction at all coverages above 2 ML [12]. III-V overlayers on Ge were synthesized as 10–30-Å-thick epitaxial layers grown at 360 °C and exhibited more complex multidomain reconstructions [12].

Angle-integrated photoelectron energy distribution curves (EDC's) were recorded using Al $K\alpha$ radiation (1486.6 eV) and an overall energy resolution of 0.7 eV. Each valence-band offset ΔE_v was determined [9] as illustrated in Fig. 1. In the inset we show valence-band spectra for a 200-Å-thick Ge epitaxial layer (top), a 200-Å-thick AlAs epitaxial layer (midsection), and a 0.5-μm-thick GaAs epitaxial layer (bottom). The binding energy scale is referenced to the valence-band maximum E_v as derived from a fit to Gaussian-convoluted theoretical density of states [13]. EDC's for the core emission from these samples are shown in Fig. 1(a). The core binding energies were measured relative to E_v for each sample, and the zero of the energy scale was taken at the position of the Ge 3*d* centroid in bulk Ge. Therefore the apparent core separation in Fig. 1(a) is that expected for hypothetical heterojunctions with zero valence-band offset.

In Fig. 1(b) we show the core emission from a representative AlAs-Ge-GaAs(001) heterostructure (for a Ge layer of 14 ML). The zero of the energy scale is at the position of the Ge 3*d* core level. The variation in the energy separation of any two core levels relative to Fig. 1(a) was independent of AlAs and Ge layer thickness in the range explored [14] and gives directly the valence band offset across the corresponding interface. We find [15] $\Delta E_v = 0.23 \pm 0.05$ eV across the overall AlAs-Ge-GaAs(001) heterostructure, with $\Delta E_v = 0.65 \pm 0.05$ eV for the AlAs-Ge interface and $\Delta E_v = -0.42 \pm 0.05$ eV for the Ge-GaAs interface. In Fig. 1(c) we show the corresponding results for GaAs-Ge-AlAs(001), i.e., the reverse growth sequence. We find [14,15] $\Delta E_v = -0.71 \pm 0.05$ eV across the overall heterostructure, with $\Delta E_v = -0.91 \pm 0.05$ eV for the Ge-AlAs interface and $\Delta E_v = 0.20 \pm 0.05$ eV for the GaAs-Ge interface.

Since the measured valence band offsets across AlAs-GaAs(001) and GaAs-AlAs(001) heterostructures, in the absence of Ge interlayers, are $\Delta E_v = 0.45 \pm 0.05$ eV and $\Delta E_v = -0.45 \pm 0.05$ eV, respectively [10], the observed deviations from the transitivity rule for AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) structures are 0.22 $\pm$0.07 and 0.26 $\pm$0.07 eV, respectively, both in the direction of raising the valence-band maximum of the III-V overlayer relative to the III-V substrate. Such de-

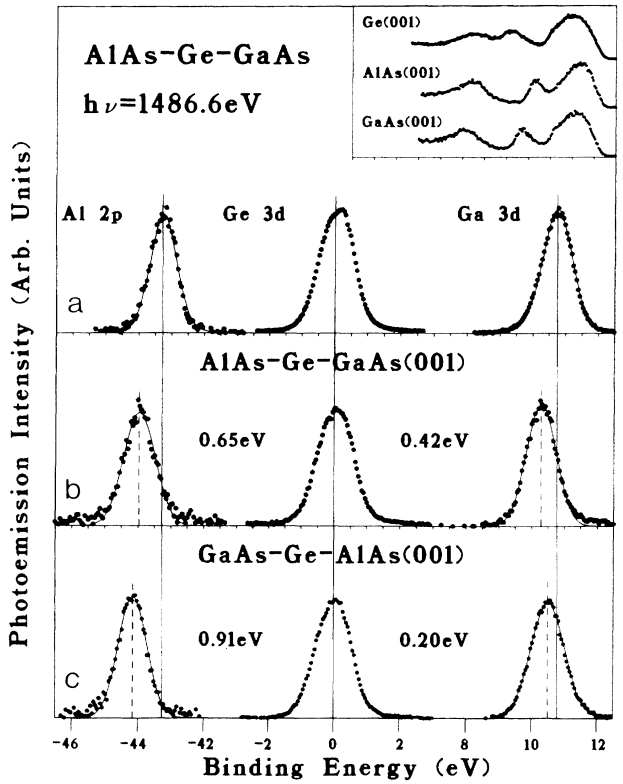

FIG. 1. Inset: Valence-band emission from Ge(001), AlAs(001), and GaAs(001) epitaxial bulk standards. (a) Al $2p$, Ge $3d$, and Ga $3d$ core emission from the same samples. The zero of the energy scale was taken at the position of the Ge $3d$ centroid and the apparent core separation is that expected from hypothetical heterojunctions with zero valence-band offset. (b) Core emission from an AlAs-Ge-GaAs(001) heterostructure. The variations in the core separation relative to (a) give directly the valence-band offsets. (c) Core emission from GaAs-Ge-AlAs(001) heterostructures.

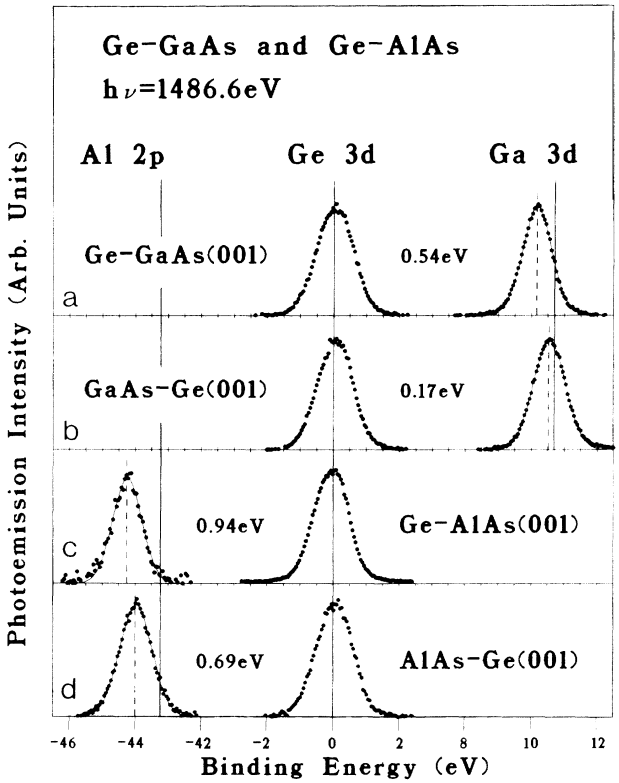

FIG. 2. Band-offset measurements in individual isolated heterojunctions. Data shown are for overlayer thicknesses of 20 Å. (a) Ge $3d$ and Ga $3d$ core emission from a Ge-GaAs(001) heterojunction. The zero of the energy scale was taken at the position of the Ge $3d$ centroid, and the solid lines give the core binding energy in bulk standards, from Fig. 1(a). The variations in core separation (see dashed vs solid vertical lines) give directly the valence-band offsets. (b) Ge $3d$ and Ga $3d$ core emission from a GaAs-Ge(001) heterojunction. (c) Al $2p$ and Ge $3d$ core emission from a Ge-AlAs(001) heterojunction. (d) Al $2p$ and Ge $3d$ core emission from an AlAs-Ge(001) heterojunction.

viations are consistent with those reported earlier for Ge layer thicknesses in the 1-2 ML range [1]. More importantly, the observed deviations, and the width of the Ge $3d$ line shape are independent of Ge thickness in the range explored (2-16 ML), a fact that is difficult to reconcile with the presence of long-range electrostatic fields across the Ge interlayer. Ideally abrupt, (001)-oriented junctions between heterovalent semiconductors would be charged [3-7]. Since long-range electrostatic fields would be incompatible with thermodynamic stability, charged interfaces could possibly exist—with opposite polarity—only across thin enough interlayers [3-7]. In contrast with the present experimental results, however, the resulting dipole field across the interlayer would monotonically change the band offset [5] and broaden the Ge $3d$ line with increasing Ge thickness.

We compared the results for single quantum wells (Fig. 1) with those of individual, isolated interfaces grown in *identical* conditions. We defined as "isolated" interfaces those found in structures where the separation between interfaces exceeds the Debye length L_D of the material. Individual n^+-Ge/III-V(001) interfaces were obtained by growing an appropriate III-V substrate layer 500-5000 Å thick ($> L_D \sim 100$-200 Å) on GaAs(001) wafers, followed by deposition of 10-30 Å of Ge at 360 °C. Individual III-V/n^+-Ge(001) interfaces were obtained by growing a n^+-Ge substrate layer ($N_D \sim 3.6\times10^{19}$ cm^{-3}) 60 Å thick ($> L_D \sim 8$ Å) at 360 °C on a GaAs buffer, followed by deposition of 10-30 Å of the appropriate III-V overlayer at 360 °C.

In Figs. 2(a)-2(d) we show EDC's for the core-level emission from such individual heterojunctions. The zero of the energy scale is taken at the position of the Ge $3d$ centroid. The vertical solid line for each core level marks the position of the core level relative to E_v in the bulk standards, from Fig. 1(a). For each interface the varia-

tion in core separation relative to Fig. 1(a) (dashed versus solid vertical line spacing in Fig. 2) gives directly the *magnitude* of the valence-band offset [16]. For Ge-GaAs(001) we find [15] $\Delta E_v = -0.54 \pm 0.05$ eV, for GaAs-Ge(001), $\Delta E_v = 0.17 \pm 0.05$ eV, for Ge-AlAs(001), $\Delta E_v = -0.94 \pm 0.05$ eV, and for AlAs-Ge(001), $\Delta E_v = 0.69 \pm 0.05$ eV. Therefore individual isolated IV/III-V interfaces, that cannot be charged, exhibit deviations from the commutativity rule [17]. Such deviations must be associated with the establishment of inequivalent local environments leading to neutral interfaces [5].

The offsets measured for isolated interfaces are compellingly similar to those obtained in III-V/Ge/III-V quantum-well structures, as shown in the uppermost section of Fig. 3. For example, if we use the measured valence-band offsets for individual neutral interfaces to estimate the behavior of AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) structures, we obtain deviations from the transitivity rule of 0.30 ± 0.07 and 0.32 ± 0.07 eV, respectively, in good agreement with the measured values of 0.22 ± 0.07 and 0.26 ± 0.07 eV from Fig. 1. We therefore conclude that, at least for Ge layer thicknesses larger than 1–2 ML, the observed deviations from the transitivity rule in III-V/Ge/III-V structures are due to the establishment of *inequivalent neutral* IV/III-V and III-V/IV interfaces rather than to the presence of *charged* interfaces.

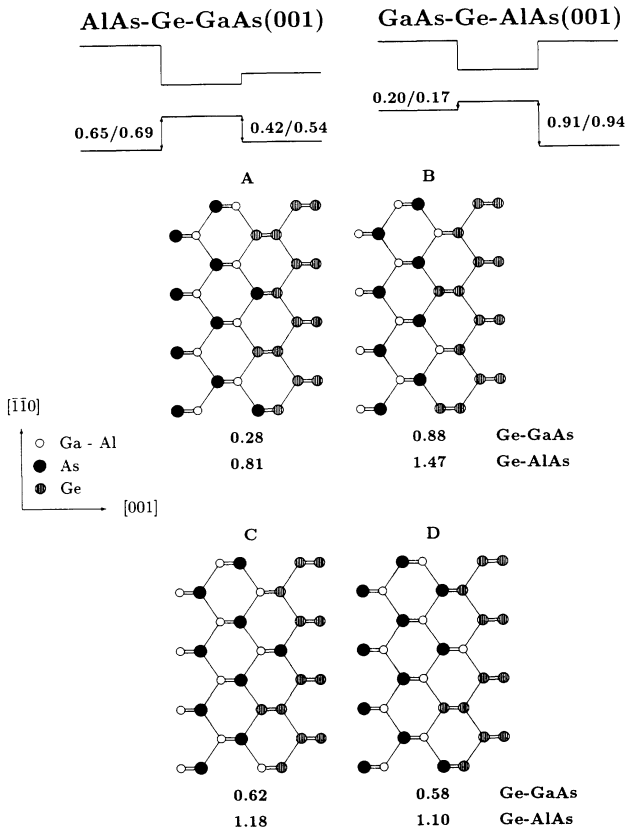

FIG. 3. Top: Experimental band offsets for the AlAs-Ge and Ge-GaAs interfaces (left) and GaAs-Ge and Ge-AlAs interfaces (right). For each interface, the first numerical value is from the results of Fig. 1 (single quantum well), and the second value from those of Fig. 2 (individual isolated interfaces). Bottom: Examples of simple interface structures that would lead to neutral interfaces. (A) Ge-As mixed termination. (B) Ge-cation mixed termination. (C) Mixed two-plane termination, 25-75 Ge-cation and 75-25 Ge-As. (D) Mixed two-plane termination, 25-75 Ge-As and 75-25 Ge-cation. Theoretical predictions for the magnitude of the valence-band offsets from self-consistent-field calculations are shown directly below the corresponding interface structure.

A few results exist in the literature [9] about the noncommutativity of band offsets in IV/III-V individual isolated heterojunctions, albeit with (110) orientation only. In particular, Zurcher and Bauer [18] and Grant *et al.* [19] reported the valence-band offset at GaAs-Ge(110) heterojunctions (0.23–0.26 ± 0.07 eV in Ref. [18], ~ 0.3 eV in Ref. [19]) to be 0.16–0.20 and 0.25 eV lower, respectively, than that reported for Ge-GaAs(110) interfaces. Extrapolating such results to a hypothetical GaAs-Ge-GaAs(110) single-quantum-well structure we would expect a deviation from the transitivity rule similar in sign and magnitude to that observed here in AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) heterostructures.

As far as the local environments corresponding to neutral inequivalent interfaces are concerned, some insight can be derived from theoretical predictions. Several authors suggested that neutral interfaces may derive from the formation of substitutional defects, e.g., through atomic diffusion across the interface, leading to interface planes of mixed composition, or through antisite formation in the III-V semiconductor region near the interface [3–5]. An example of some of the simplest possible resulting environments—in which atomic rearrangement involves only one or two atomic planes—are shown in the bottom of Fig. 3, viewed in the $(\bar{1}10)$ plane. Configurations A and B correspond to a mixed Ge-As or Ge-cation plane with 50-50 composition at the interface, respectively [4,5]. Configuration C includes two mixed planes in sequence with Ge-cation 25-75 and Ge-As 75-25 composition, and configuration D is the complementary configuration, in which the cation and anion sublattices are interchanged.

We performed first-principles self-consistent-field calculations within the local-density approximation to density-functional theory, using norm-conserving pseudopotentials, plane-wave basis sets, and supercells containing 12 or 24 atoms [5]. The predicted valence-band offsets are shown directly below each interface configuration. Configurations A and B would correspond to offsets of sensibly different magnitude. Configurations C and D have no ionic dipole, as would be the case for the nonpolar (110) orientation. Within linear response theory the corresponding band offsets are equal to one another and to the offsets for (110)-oriented interfaces. Formation of antisite defects leading to neutral interfaces

is also expected to yield offset values similar to those obtained for (110)-oriented interfaces. Both for GaAs-Ge(001) and AlAs-Ge(001) interfaces, good agreement between theory ($|\Delta E_v| = 0.28$ and 0.81 eV, respectively) and experiment ($|\Delta E_v| = 0.17$–0.20 and 0.65–0.69 eV, respectively) is found for a type-A interface configuration (mixed Ge-As interface). For Ge-GaAs(001) and Ge-AlAs(001) interfaces, good agreement between theory ($|\Delta E_v| = 0.58$–0.62 and 1.10–1.18 eV, respectively) and experiment ($|\Delta E_v| = 0.42$–0.54 and 0.91–0.94 eV, respectively) is found for a type-C or -D interface. We emphasize, however, that the interface structures considered are only some of the simplest structures which would lead to agreement between theory and experiment.

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[9] See, for example, A.D. Katnani, in *Heterojunction Band Discontinuities: Physics and Device Applications*, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987), p. 115, and references therein.

[10] See, for example, the recent results for AlAs-GaAs(001) and GaAs-AlAs(001) by K. Hirakawa, Y. Hashimoto, and T. Ikoma, Appl. Phys. Lett. **57**, 2555 (1990), who found $|\Delta E_v| = 0.44 \pm 0.05$ eV, and E. T. Yu, D. H. Chow, and T. C. McGill, J. Vac. Sci. Technol. B **7**, 391 (1989), who found $|\Delta E_v| = 0.46 \pm 0.07$ eV, for both growth sequences.

[11] See, for example, L. J. Brillson, in *Handbook on Semiconductors*, edited by P. T. Landsberg (Elsevier, Amsterdam, 1992), Vol. 1, 2nd ed., Chap. 8.

[12] See S. Strite *et al.*, Appl. Phys. Lett. **56**, 1673 (1990); and J. H. Neave *et al.*, J. Vac. Sci. Technol. B **1**, 668 (1983). Growth temperatures were monitored here with a calibrated optical pyrometer. Temperatures quoted in Ref. [1] for Ge growth were monitored with a thermocouple, and should be corrected upward by 50–60 °C.

[13] The theoretical density of states were those calculated by J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **14**, 556 (1976). A GaAs density of states was used for both GaAs and AlAs, as in Refs. [9] and [10]. The full width at half maximum of the Gaussian broadening function was 0.7 eV.

[14] For III-V overlayers we examined overlayer thicknesses in the 10–30 Å range with consistent results. Variations in Ge layer thickness in the 2–16 ML range examined, yielded no variation in the Al $2p$-Ga $3d$ core separation. The Ge $3d$-Al $2p$ and Ge $3d$-Ga $3d$ core separations could be reliably determined only for Ge coverages in the 4–16 ML range, and were independent of Ge thickness in the 4–8 to 16 ML range.

[15] The sign of the valence-band offset is taken here as positive when the valence-band maximum in the overlayer is *below* that of the substrate. Quoted errors correspond to the standard deviation of the distribution of experimental results.

[16] The variation in core separation was independent of overlayer thickness in the coverage range explored (typically 10–30 Å).

[17] Many results for Ge/GaAs interfaces have been reported in the past. A partial list of recent results for *epitaxial* systems includes, for Ge/GaAs(001): (a) J. M. Ballingall, C. E. C. Wood, and L. F. Eastman, J. Vac. Sci. Technol. B **1**, 675 (1983); (b) J. R. Waldrop *et al.*, Surf. Sci. **132**, 513 (1983); (c) A. D. Katnani *et al.*, Phys. Rev. B **31**, 2146 (1985); (d) A. D. Katnani and R. S. Bauer, Phys. Rev. B **33**, 1106 (1986); (e) S. A. Chambers and T. J. Irwin, Phys. Rev. B **38**, 7484 (1988); and (f) M. S. Ünlü *et al.*, Appl. Phys. Lett. **56**, 842 (1990), who reported values of $|\Delta E_v|$ as low as $0.39 + 0.07$ eV and as high as 0.68 ± 0.01 eV. For Ge/AlAs(001), $|\Delta E_v| = 0.78 \pm 0.07$ eV was reported in (d).

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