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AlAs-GaAs heterojunction engineering by means of group-IV elemental interface layers

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Valence- and conduction-band discontinuities in AlAs-GaAs heterostructures can be continuously tuned through fabrication of pseudomorphic elemental Ge or Si layers of controlled thickness at the interface. The local interface dipole associated with the group-IV interface layer can be added to or subtracted from the natural band offsets depending on the growth sequence. Comparison of high-resolution x-ray-photoemission studies of AlAs-Ge-GaAs and AlAs-Si-GaAs heterostructures prepared *in situ* by molecular-beam epitaxy as a function of the interface concentration of group-IV elements shows qualitative similarities and surprising quantitative differences. The observed dipole per group-IV atom is 3 times as large for Ge as for Si, but the total maximum dipole achievable at the interface is identical (0.4 eV), within experimental uncertainty, for the two group-IV elements.

Valence- and conduction-band discontinuities in semiconductor heterojunctions control carrier injection and confinement at the junction, and the ability to engineer such parameters would offer an important degree of freedom in device design.[1-8] The methods recently proposed to change valence- and conduction-band offsets[7-10] are based on the establishment of an electrostatic dipole on an atomic scale through the fabrication of a microscopic capacitor at the metallurgical interface. For example, total-energy calculations of the effect of group-IV bilayers at III-V/III-V semiconductor interfaces,[7,8] as well as group-III-V layers in IV/IV junctions[10] have predicted the establishment of a n^+-p^+ double layer with a change in valence- and conduction-band offsets of the order of 1 eV. In this paper we present an experimental study of the effect of lattice-matched pseudomorphic Ge layers on the AlAs-GaAs band offset and the first demonstration that a Ge-induced local dipole can be added to or subtracted from the natural band offset depending on the growth sequence. A comparison of our results for the lattice-matched AlAs-Ge-GaAs system with our results for AlAs-Si-GaAs (Refs. 5 and 9) allowed us to identify systematic trends which challenge the present understanding of the microscopic mechanisms responsible for offset tuning. First, the local interface dipole initially increases with the number of group-IV atoms about 3 times as fast for Ge as for Si. Second, the maximum total dipole observed is identical, within experimental uncertainty, for Ge and Si. Consequently, the nominal thickness of the interface layer at which saturation of the local dipole is observed is a factor of 3 smaller for Ge as compared to Si. Existing theoretical models based on the formation of an abrupt group-IV bilayer at the interface are insufficient to explain such quantitative trends, albeit they account for the direction and order of magnitude of the dipole.[7,8,10]

AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) heterostructures were fabricated by conventional solid source molecular-beam epitaxy (MBE) technology in a multichamber system, described elsewhere,[9] which includes an analysis chamber with monochromatic x-ray photoemission spectroscopy (XPS) capabilities. Reflection high-energy electron diffraction (RHEED) was used to monitor long-range order and calibrate the III-V growth rate through RHEED intensity oscillations. As-stabilized 2×4 reconstructed GaAs(001) substrates or As-stabilized 3×1 reconstructed AlAs(001) substrates were fabricated on GaAs(001) wafers following the methodology described in Refs. 5 and 9. We employed undoped substrates, as well as n-doped (Si-doped, $n=1\times10^{18}$ cm^{-3}) substrates with identical results.

To obtain a Ge layer of a given thickness, the growth of the substrate was stopped by closing the group-III element shutter while leaving the As shutter open; the substrate temperature rapidly lowered to 280 °C, and the shutter of the Ge effusion cell opened for a calibrated time interval. The AlAs-Ge-GaAs(001) and GaAs-Ge-AlAs(001) heterostructures to be used for band offset determination were completed by growing thin (15–30 Å thick) overlayers of the appropriate type at 280 °C on top of the Ge interface layer. For selected Ge thicknesses, an alternate growth procedure was examined in which no As flux was employed during Ge deposition (background pressure during deposition $<5\times10^{-10}$ Torr). Interface layer thickness and the resulting band offsets were found to be consistent, within experimental uncertainty, for samples fabricated with the two procedures, although the two deposition procedures corresponded to qualitatively different RHEED patterns from the Ge layer.[11]

Photoelectron energy distribution curves (EDC's) at a photon energy of 1486.6 eV for the Ge 3*d* and Ga 3*d* core emission features as a function of coverage (Fig. 1) were used to calibrate the Ge deposition rate and the Ge coverage in monolayers (1 ML$=6.25\times10^{14}$ atoms/cm^2). The observed exponential attenuation of the Ga 3*d* emission with Ge coverage, and complementary exponential increase in the Ge emission (inset of Fig. 1),[12] with attenuation length given by the photoelectron escape depth (15 Å, Ref. 13) were fully consistent with those expected for layer-by-layer growth of an unreacted Ge overlayer. The resulting coverages were confirmed by *ex situ* measure-

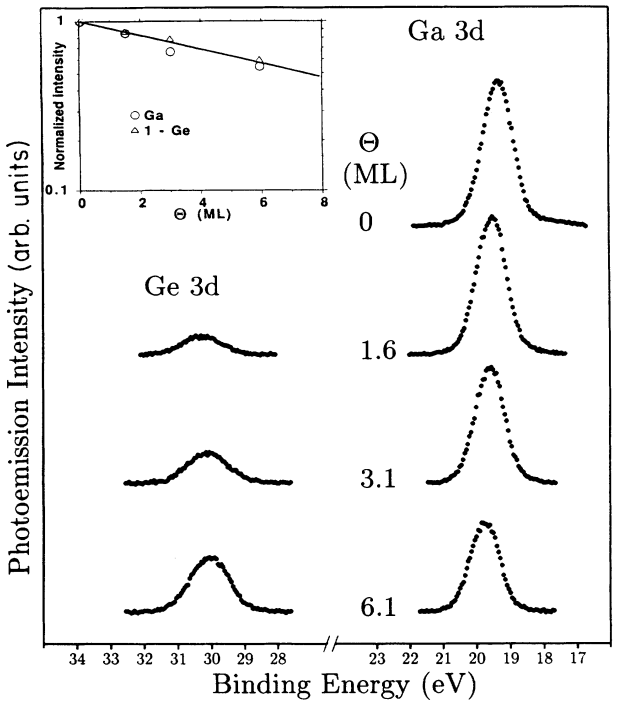

FIG. 1. Ge 3*d* and Ga 3*d* core emission from Ge-GaAs(001) interfaces grown at 280 °C and exhibiting sharp 2×2 RHEED patterns. In the inset, we plot on a logarithmic scale the integrated photoemission intensity of the Ga 3*d* core levels $I_{Ga}(\theta)$, normalized to the initial intensity prior to Ge deposition $I_{Ga}(0)$, as a function of Ge coverage (open circles). In the same inset, we also plot the corresponding logarithmic values of $1-I_{Ge}(\theta)/I_{Ge}(\infty)$ (open triangles), where $I_{Ge}(\theta)$ is the integrated emission intensity of the Ge 3*d* core level at a Ge coverage θ, and $I_{Ge}(\infty)$ is the high coverage limit of the Ge-integrated emission intensity.

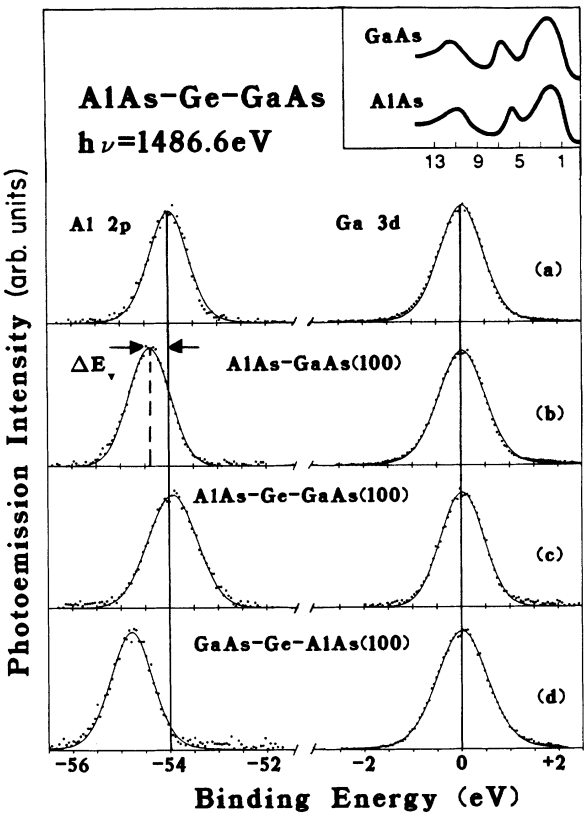

FIG. 2. The inset shows the valence-band emission from GaAs(100) and AlAs(100) epitaxial layers. (a) Al 2*p* and Ga 3*d* core emission from the same samples. The zero of the energy scale was taken at the position of the Ga 3*d* cores in GaAs and the apparent core separation is that expected from a hypothetical heterojunction with zero valence-band offset. (b) Core emission from an AlAs-GaAs(100) heterojunction for an AlAs thickness of 15 Å. The variation in the core separation relative to (b) gives directly the valence-band offset of 0.42 ± 0.08 eV. (c) Core emission from an AlAs-GaAs(100) heterostructure with a 0.15-ML Ge interface layer and an AlAs thickness of 15 Å. The corresponding valence-band offset is -0.03 ± 0.08 eV. (d) Core emission from a GaAs-AlAs(100) heterostructure with a 0.15-ML Ge interface layer and a GaAs thickness of 15 Å. The corresponding valence-band offset is 0.79 ± 0.08 eV.

ments of thick films by means of a profilometer, within an experimental uncertainty of 15%. The Ge overlayers exhibited all sharp, single-domain RHEED patterns,[11] consistent with those recently reported by Strite *et al.*[14] The growth of thin III-V overlayers at 280 °C on top of the Ge layer to fabricate III-V/IV/III-V heterostructures for band offset measurements yielded more complex RHEED patterns associated with multidomain 2×4 reconstructions.[11]

We used XPS *in situ* to determine the effect of the Ge interface layer on the AlAs-GaAs valence-band offset. The valence-band offset ΔE_v was measured from the position of the Ga 3*d* or Al 2*p* core levels relative to the valence-band maximum E_v in the substrate, the position of the cation core levels relative to the valence-band maximum in thick (200 Å) overlayers, and the energy difference of the Al 2*p* and Ga 3*d* core levels at the interface.[15] Representative EDC's are shown in Fig. 2. In the inset, we show valence-band spectra for a 0.5-μm thick GaAs epitaxial substrate (top) and a 200-Å thick AlAs epitaxial layer (bottom). The binding-energy scale is referenced to the valence-band maximum E_v as derived from a least-squares linear fit of the leading valence-band edge. EDC's for the Al 2*p* and Ga 3*d* emission from these two samples[16] are shown below the inset in Fig. 2(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 Ga 3*d* centroid in GaAs. Therefore the apparent core separation is that expected from a hypothetical heterojunction with zero valence-band offset. In Fig. 2(b) we show core EDC's from AlAs-GaAs(100) for an AlAs thickness of 15 Å, in the absence of any Ge interface layer. The variation in the core separation relative to the results in Fig. 2(a) is independent of AlAs thickness in the thickness range examined here (10–30 Å) and gives directly the AlAs-GaAs(100) heterojunction valence-band offset (0.42 ± 0.08 eV). The same offset (0.46 ± 0.08) is found, within experimental uncertainty, for the GaAs-AlAs(100) heterojunction in the absence of a Ge interface layer.[17]

In Figs. 2(c) and 2(d) we show core EDC's for AlAs-GaAs and GaAs-AlAs heterostructures in the presence of a Ge interface layer of 0.15 ML. The core separation reflects valence-band offsets of -0.03 ± 0.08 and $+0.79 \pm 0.08$ eV, respectively. We emphasize that the relatively short experimental sampling depth employed[13] rules out artifacts due to depletion layer variations. Measured valence-band offsets as a function of Ge interface layer thickness are summarized in the topmost section of Fig. 3 for a number of AlAs-Ge-GaAs(001) (solid circles) and GaAs-Ge-AlAs(001) (open circles) heterostructures. The relatively symmetric behavior of the data suggest that a Ge-induced dipole is subtracted from the natural valence-band offset in AlAs-GaAs(001) heterostructures, and added to the offset in GaAs-AlAs(001) heterostructures. The magnitude of the dipole increases linearly with nominal interlayer thickness up to a maximum value of about 0.4 eV at 0.15 ML, and decreases slowly for higher Ge coverages. Photoemission techniques cannot probe directly the conduction-band discontinuity. The theoretical models of Refs. 7,8, and 10 predict that the presence of a group-IV-induced dipole would not change the AlAs-GaAs band-gap difference, so that an increase in valence-band offset in Fig. 3 would be accompanied by a parallel decrease in the conduction-band offset, and vice versa.

The results in the topmost section of Fig. 3 exhibit compelling qualitative similarities together with important quantitative differences relative to those obtained with Si interface layers in analogous structures. For comparison, we show in the lower section of Fig. 3 the corresponding results for AlAs-Si-GaAs(001) (solid circles) and GaAs-Si-AlAs(001) (open circles) heterostructures, from Ref. 5. If one defines here, for simplicity, the total dipole as the modification of the valence-band offset resulting from the presence of the group-IV layer, and the specific dipole as the offset modification per group-IV atom, then Ge exhibits a maximum total dipole identical, within experimental uncertainty, to that of Si (0.4 eV), but a specific dipole about 3 times as large as that of Si.

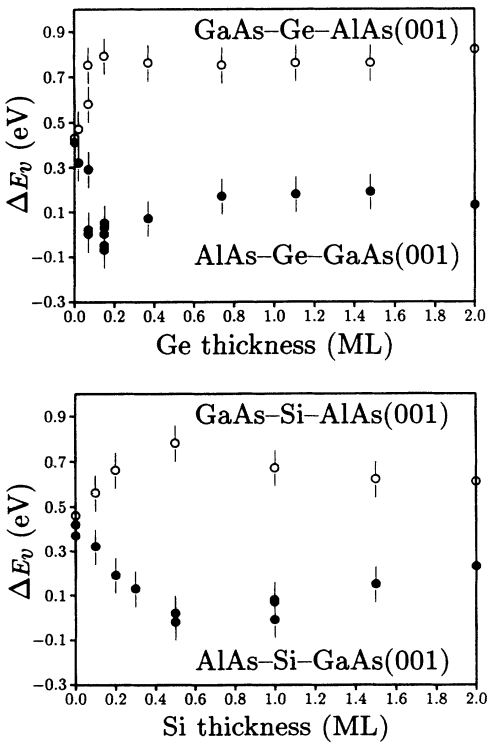

FIG. 3. The valence-band offset ΔE_v for AlAs-GaAs heterostructures as a function of the thickness of an ordered Ge (top) or Si (bottom) layer at the interface. The layer is grown in both cases on an As-stabilized substrate surface.

Such trends challenge our understanding of the microscopic mechanism responsible for the dipole. Recent *ab initio* self-consistent calculations[7,8] predicted that abrupt Ge bilayers at GaAs-GaAs homojunctions should induce valence-band offsets due to a charge transfer (prior to dielectric screening) of about -1 electron per atom in the Ge monolayer which "replaces" Ga in the structure, and $+1$ electron per atom in the Ge monolayer replacing As atoms. Calculations by Peressi *et al.*[10] examined AlAs-Si-GaAs(001), GaAs-Si-AlAs(001), AlAs-Ge-GaAs(001), and GaAs-Ge-AlAs(001) assuming that the group-IV atoms are uniformly distributed over two consecutive atomic layers at all coverages to ensure local charge neutrality, the appropriate effective inverse dielectric constant is that of an hypothetical bulk alloy with the same composition as the doped bilayer, and the III-V overlayer growth is cation initiated also on top of the group-IV interlayer.[18]

Under these assumptions, the model by Peressi *et al.*[10] yields the correct direction and order of magnitude of the dipole for all systems. In particular, we would expect the dipole to act as to reduce the AlAs-GaAs(100) valence-band offset and increase the GaAs-AlAs(100) offset, since the group-IV interface layer is always grown on an As-terminated substrate surface, and overlayer growth is cation initiated in both cases (see, however, Ref. 18). In other words, the n^+-p^+ dipole maintains the same orientation, when the two semiconductors are interchanged. The calculations by Peressi *et al.*[10] furthermore quantitatively reproduce the effect of Si interface layer of thickness up to 0.5 ML but show a degraded quantitative agreement with the case of Ge. The predicted specific dipole of Ge is essentially the same as that of Si (Ref. 10), while we experimentally observe an increase of a factor of 3 in the case of Ge.

More importantly, on the basis of the theoretical models one would expect a maximum total dipole of 0.97 (Ref. 8) or 1.3 eV (Ref. 10) for Ge and 1.4 eV for Si, at a coverage of two monolayers, when the n^+-p^+ interface dipole layer is completed. We observe, instead, an identical maximum dipole of about 0.4 eV at coverages of 0.15 and 0.5 ML, respectively, for Ge and Si. This value of the maximum dipole is compellingly similar to that observed by McKinley *et al.*[19] during studies of As-Ga and Ga-As interface double layers in Ge-Ge homojunctions. Band offsets of 0.35–0.45 eV and an opposite sign for "Ga-first" versus "As-first" growth sequences were reported, to be compared with the theoretical values of 0.69 eV expected from the n^+-p^+ doping interface dipole limit for a (111) near interface, or 2.07 eV for a (111) far interface.[4,20]

We propose that the existence of a maximum interface

dipole of identical magnitude for AlAs-Ge-GaAs, GaAs-Ge-AlAs, Ge-GaAs-Ge, Ge-AsGa-Ge, AlAs-Si-GaAs, and GaAs-Si-AlAs, with quite different interface layer thicknesses, represents the most stringent criterion to date for the validity of theoretical models of interface dipole formation. Many of the mechanisms that one can devise to explain the local dipole saturation [strain induced interface chemical roughness,[5] antisite defect formation,[10] δ-doping effects,[4] transition from cation to anion initiated III-V overlayer growth (i.e., antiphase domain formation, Refs. 14 and 18), Si or Ge thermally activated diffusion, etc.] fail to meet this test. For example, the similar maximum dipole for interface layers of Si and Ge, which exhibit widely different strain, diffusivity, and self-compensation in III-V materials, argues against strain, diffusion, and δ-doping related effects. The similarity of the results for III-V/IV/III-V and IV/III-V/IV structures argues against antisite defects and antiphase domain formation limiting the maximum dipole, since these do not form in IV/IV junctions. We speculate that the answer may come from models incorporating cation or anion swaps[7,20] across the interface to counteract the effect of a critical group-IV-induced interface electrostatic field,[21] that reaches values of $2-3\times10^7$ V/cm at the maximum dipole for all of the heterostructures examined.

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[11]More details will be provided in a longer forthcoming paper.

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[16]The data (solid circles) are shown superimposed to the result of a least-squares fit in terms of a single Gaussian-convoluted Lorentzian line, which is intended only as a guide to the eye. Centroids were used to determine the core binding energies.

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[18]The latter obviously is the actual growth mode in the absence of the group-IV interface layer, and is therefore likely to remain the actual growth mode also at the lowest Ge or Si coverages explored, but for higher Ge or Si thickness the situation may be different. See F. D. Bringans, M. A. Olmstead, F. A. Ponce, D. K. Biegelsen, B. S. Krusor, and R. D. Yingling, J. Appl. Phys. **64**, 3472 (1988), and references therein.

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