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Tuning AlAs-GaAs band discontinuities and the role of Si-induced local interface dipoles

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The presence of thin ordered layers of Si within the interface region of AlAs-GaAs heterostructures is found to tune the valence-band offset throughout the 0.02–0.78 eV range. High-resolution x-ray-photoemission studies of heterostructures prepared *in situ* by molecular-beam epitaxy as a function of substrate temperature, arsenic flux, interface concentration of Si, and growth sequence (AlAs on GaAs versus GaAs on AlAs) indicate that this tunability is associated with a Si-related local dipole which can be added to or subtracted from the intrinsic AlAs-GaAs valence-band offset of 0.40 eV.

Recent *ab initio* self-consistent calculations[1] and linear-response-theory results[2] examining the effect of polar layers on heterojunction band offsets have focused attention on the stability and electrostatics of group-IV elemental bilayers at polar interfaces between III-V semiconductors. For example, ideally abrupt Ge bilayers at GaAs-GaAs model polar interfaces are expected to give rise to local dipoles and induce valence-band offsets of 0.7–1.0 eV (Ref. 1). Changes of such magnitude in the valence- and conduction-band lineups, if obtainable in practice, would have important technological applications.[3]

We present here an experimental study of the effect of Si interface layers on the AlAs-GaAs heterojunction band offset, and demonstrate that a single-interface chemical species can cause either an increase or a decrease in heterojunction band offsets depending on growth conditions. Relative to the GaAs-Si-GaAs model system considered in Ref. 1, the choice of the AlAs-Si-GaAs and GaAs-Si-AlAs systems offers several experimental advantages. First, the difference in cation species across the heterojunctions greatly simplifies the task of determining band offsets by means of photoemission spectroscopy. Second, the diffusion coefficient of Si in GaAs is substantially lower than that of Ge, reducing the importance of impurity redistribution.[4] Third, the literature about Si δ-doping technology[5] in III-V materials is far more extensive than that concerning Ge. Strain effects, however, are expected to be larger for Si interface layers.

The experiments were conducted in a recently established facility which includes a Riber 32*P* molecular beam epitaxy (MBE) chamber for the growth of III-V semiconductors and a Riber 32*P* MBE chamber for the growth of II-VI semiconductors, interconnected with a monochromatic x-ray-photoemission (XPS) spectrometer (1486.6 eV, overall energy resolution 0.69 eV).

All structures were grown on undoped GaAs(100) wafers etched in a $5NH_4OH:2H_2O_2:10H_2O$ solution, and then heated at 580 °C in UHV to remove the oxide. On this substrate 0.5-μm-thick *n*-type (Si doped, 6×10^{17} cm^{-3}) GaAs buffer layers were grown at a temperature of 620 °C with a typical As partial pressure of 8×10^{-6} Torr. Growth was monitored by reflection high-energy electron diffraction (RHEED), and the growth rate calibrated by means of RHEED intensity oscillations. GaAs growth proceeded on the As-stabilized 2×4 surface, at a typical rate of 1 μm/h. Measured electron mobilities of lightly doped *n*-type test samples (Si doped, 10^{14} cm^{-3}) grown in these temperature and flux conditions were typically in the 80 000 cm^2/Vs range at 77 K. AlAs-GaAs heterostructures for band-offset measurements were formed by growing 15–20-Å-thick AlAs epitaxial overlayers on GaAs(100) substrates. GaAs-AlAs heterostructures for band-offset measurements were fabricated by growing 15–20-Å-thick epitaxial GaAs overlayers on a 200-Å-thick undoped AlAs(100) epitaxial substrate exhibiting the As-stabilized 3×1 reconstruction. The AlAs layer was also grown at 620 °C on the GaAs buffer.

The Si interface layers were obtained by stopping the growth of the substrate material by closing the group-III-element shutter and leaving the As shutter open. For Si deposition, substrate temperatures throughout the 240–540 °C range were employed with identical results. With increasing Si coverage an intermediate 2×1 reconstruction was observed, followed by a transition to the final 3×1 reconstruction observed in earlier δ-doping studies.[4] Upon completion of a given Si coverage, the Si shutter was closed, the substrate temperature was raised to the desired temperature, and overlayer growth was started by opening the Ga or Al shutter. Si coverages were determined through flux calibrations performed on homogeneously doped GaAs layers, and are given here in monolayers (ML), in terms of the GaAs(100) surface atomic density (1 ML $=6.25\times10^{14}$ atoms/cm^2).

Large Si flux miscalibrations or redistribution effects were ruled out by monitoring the Ga 3*d* and Si 2*p* integrated core-photoemission intensity in Si-GaAs as a function of Si coverage in the 2–8 ML range, and monitoring the attenuation of the Si 2*p* and Ga 3*d* core emission as a function of AlAs thickness in AlAs-Si-GaAs.[6] The results indicate that the Si coverage is consistent with the flux calibration within an experimental uncertainty of about 15%, and that most of the Si atoms remain at the interface. In the range of growth temperatures employed

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here, relatively abrupt Si profiles have been observed in GaAs during Si δ-doping experiments.[7] No previous results are available, to our knowledge, for Si layers at AlAs-GaAs interfaces, where our data suggest even more abrupt profiles to be achieved, possibly due to segregation effects.

The valence-band offset ΔE_v was measured from the position of the Ga 3d or Al 2p 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 2p and Ga 3d core levels at the interface.[8] Representative angle-integrated photoelectron energy distribution curves (EDC's) are shown in Fig. 1. 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). EDC's for the Al 2p and Ga 3d emission from these two samples are shown in Fig. 1(a), immediately below the inset.[9] We show the zero of the binding-energy scale in Fig. 1(a) at the Ga 3d position in GaAs. The core positions referenced to E_v for each sample are 72.86 ± 0.05 and 18.86 ± 0.05 eV, respectively, in agreement with the literature.[10] The apparent core-energy separation in Fig. 1(a) is therefore that expected in a heterojunction for zero valence-band offset. In Fig. 1(b) we show core EDC's from AlAs-GaAs(100) for an AlAs thickness of 15 Å, in the absence of any interface Si layer. The variation in the core separation relative to the results in Fig. 1(a) is independent of AlAs thickness in the thickness range of interest here (3–30 Å) and gives directly the AlAs-GaAs(100) heterojunction valence-band offset (0.40 ± 0.07 eV). The same offset is found, within experimental uncertainty, for the GaAs-AlAs (100) heterojunction in the absence of a Si interface layer, in agreement with the results of Katnani and Bauer.[10]

In Figs. 1(c) and 1(d) we show core EDC's for AlAs-GaAs and GaAs-AlAs heterostructures in the presence of a Si interface layer of 0.5 ML. The variations in core separation reflect valence-band offsets of 0.02 ± 0.07 and 0.78 ± 0.07 eV, respectively. We emphasize that no changes in core line shapes are observed as a result of the presence of Si interface layers, i.e., only a rigid change of the core separation is detected. This, together with the experimental sampling depth employed,[11] rules out artifacts due to depletion-layer variations or interface reactions.

Experimental results for twelve AlAs-GaAs(100) and seven GaAs-AlAs(100) heterostructures (solid triangles and circles, respectively) are summarized in Fig. 2. The data indicate that a Si-induced local dipole is subtracted from the intrinsic heterojunction valence-band offset in AlAs-GaAs(100) heterostructures, and added to the intrinsic value in GaAs-AlAs(100) heterostructures. The magnitude of the dipole depends on the Si coverage, reaches a maximum of 0.38 eV at about 0.5 ML, and decreases slowly at higher Si coverages.

The observed Si-related dipole is consistent in sign and order of magnitude with that expected from an extrapolation of the theoretical results of Ref. 1, but the Si-coverage dependence of the dipole is markedly different from that expected on the basis of the same analysis. For

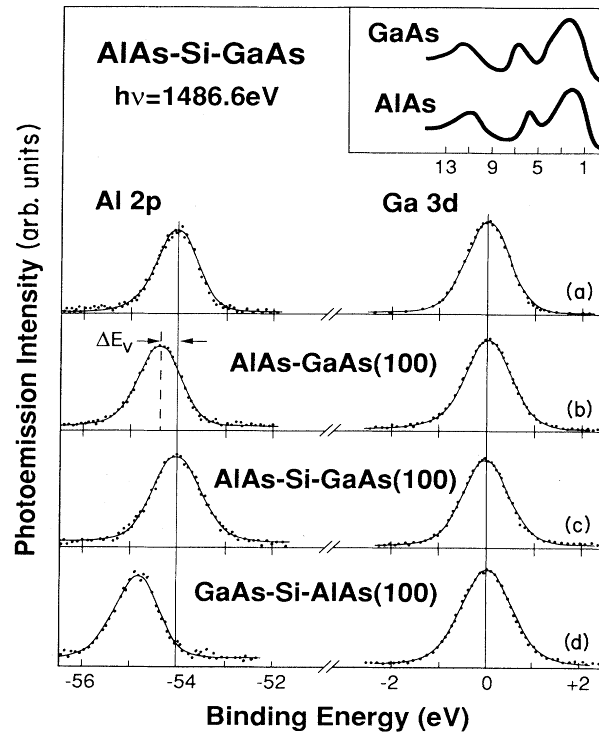

FIG. 1. Inset: Valence-band emission from a 0.5-μm-thick GaAs(100) buffer layer (top) and a 200-Å-thick AlAs(100) layer (bottom) epitaxially grown on GaAs at 620 °C. The binding-energy scale is referenced to the valence-band maximum E_v as derived from a least-squares linear fit of the leading valence-band edge. (a) Al 2p and Ga 3d core emission from the same samples (see Ref. 12). 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 3d cores in GaAs (18.86 ± 0.05 eV below E_v). Therefore, the apparent core separation is that expected from a hypothetical AlAs-GaAs heterojunction with zero valence-band offset. (b) Al 2p and Ga 3d core emission from an AlAs-GaAs(100) heterojunction for an AlAs thickness of 15 Å. The variation in the core separation relative to (a) gives directly the valence-band offset of 0.40 ± 0.07 eV, in agreement with the results of Ref. 13. (c) Core emission from an AlAs-GaAs(100) heterostructure with a 0.5-ML Si interface layer and an AlAs thickness of 15 Å. The corresponding valence-band offset is 0.02 ± 0.07 eV. (d) Core emission from a GaAs-AlAs(100) heterostructure with a 0.5-ML Si interface layer and a GaAs thickness of 15 Å. The corresponding valence-band offset is 0.78 ± 0.07 eV.

ideal, abrupt GaAs-Ge-GaAs(100) heterostructures involving Ge bilayers, Muñoz, Chetty, and Martin[1] calculated a charge transfer per Ge atom (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, so that the Ge bilayer will effectively act as a n^+-p^+ layer at the junction. The corresponding calculated dipole (and valence-band offset) is 0.97 eV. Extrapolating this result to the AlAs-Si-GaAs system, but still neglecting strain effects, we would expect a similar charge transfer and dipole,

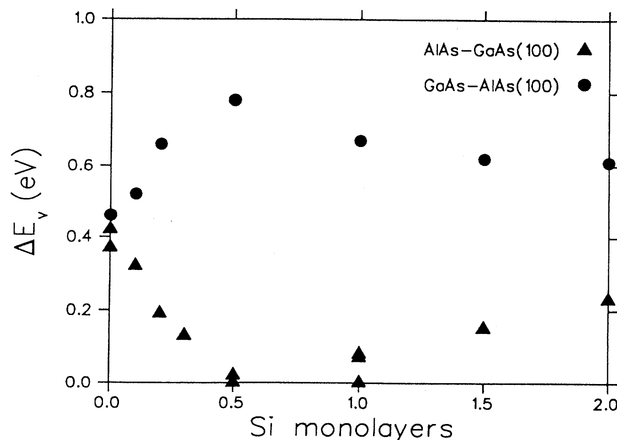

FIG. 2. Valence-band offset ΔE_v for AlAs-GaAs(100) and GaAs-AlAs(100) heterostructures (solid triangles and circles, respectively) as a function of the thickness of an ordered Si layer at the interface. The layer is grown in both cases on an As-stabilized substrate surface. A Si-induced local interface dipole is subtracted from or added to, respectively, the intrinsic valence-band offset of 0.40 ± 0.07 eV. Control of the Si coverage, growth sequence, and As flux yields a valence-band offset continuously tunable in the 0.02–0.78 eV range.

since the dielectric screening of GaAs can be replaced by the harmonic average of that of AlAs and GaAs without substantial change in the resulting dipole.[12] More importantly, we would expect the dipole to act as to reduce the AlAs-GaAs(100) valence-band offset and increase the GaAs-AlAs(100) offset, if the Si interface layer is always grown on an As-terminated substrate surface, and overlayer growth is cation initiated in both cases. This is indeed what is observed (Fig. 2). The reduced magnitude of the dipole (0.4 eV relative to 0.97 eV) could be explained by strain effects, and/or by the difficulty of obtaining, in practice, ideally abrupt interfaces.

A word of caution is required here. The direct applicability of the model by Muñoz *et al.*[1] rests on the cation-initiated nature of overlayer growth. While this is the experimental growth mode in the absence of Si (Ref. 4), and is likely to be the actual growth mode also in the presence of Si coverages well below a monolayer, the situation is less clear for higher Si coverages. Studies of the early stages of GaAs epitaxial growth on bulk Si reveal that on Si(111) islands of GaAs appear separated by As-terminated Si regions, while on Si(100) the area between the islands is not As terminated, but consists of a thin layer which probably contains both Ga and As atoms.[13] We conclude that it is not possible to assume *a priori* that in the presence of a Si interface layer the growth of the III-V overlayer will be cation initiated in all cases, and that, in principle, the atomic structure of the interface may not exactly coincide with an extension of the model by Muñoz *et al.*[1]

Based on the results of Ref. 1 we would predict a maximum Si-related dipole for a Si coverage of two monolayers, at which the n^+-p^+ layer is completed. We observe instead a maximum dipole at 0.5 ML, decreasing slowly in the 1–2 ML range. Throughout this coverage range the 3×1 RHEED pattern remains unchanged, indicating that long-range order is not perturbed. We examined the temperature dependence of these results for AlAs-Si-GaAs. We obtained identical results for GaAs substrate temperatures as low as 240 °C and as high as 540 °C during Si deposition. We speculate that the strain resulting from Si surface coverages exceeding 0.5 ML may result in chemical roughness[14] of the Si/III-V semiconductor interfaces, with a corresponding reduction of the local dipole.

Other models based on Schottky-like corrections to the heterojunction band lineup or electronegativity arguments have been recently proposed to explain the effect of submonolayer amounts of metallic impurities at semiconductor heterojunctions involving nonpolar semiconductor surfaces and amorphous overlayers.[15] Such models cannot be easily extrapolated to the present case, which involves polar substrate surfaces, epitaxial overlayers, and most of all interlayers of a nonmetallic element with amphoteric character in both of the semiconductors involved.

In conclusion, Si layers grown in the interface regions of AlAs-GaAs heterostructures remain mostly located at the interface, exhibit long-range order, and give rise to a local dipole as large as 0.38 eV. Depending on the growth sequence and Si concentration, the dipole can be exploited to continuously tune the valence-band offset in the 0.02–0.78 eV range. Theoretical models recently proposed to predict stability and electrostatics of group-IV elemental layers at III-V semiconductor heterojunctions can account for direction and order of magnitude of the dipole, but fail to explain the Si concentration dependence of the dipole.

Note added in proof. Self-consistent supercell calculations of the band lineups using the local-density approximation, norm-conserving pseudopotentials, and plane-wave basis sets have been performed for AlAs-Si-GaAs and GaAs-Si-AlAs by Peressi, Baroni, Resta, and Baldereschi.[16] Assuming that Si atoms are uniformly distributed over two consecutive atomic layers to ensure local charge neutrality, remarkable quantitative agreement with our results is obtained up to a coverage of 0.5-ML Si. The departure of the measured offset from theoretical predictions at higher coverages is attributed to Si diffusion.

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