Artificial band discontinuities at GaAs homojunctions

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(Received 2 July 1992)

Valence- and conduction-band offsets can be induced at GaAs(100) polar homojunctions by means of ultrathin Si intralayers. The microscopic interface dipole responsible for the creation of such offsets can be varied by changing the Si intralayer thickness; the consequently variable band discontinuities represent a tunable parameter with potential applications in band-gap engineering. Even though the existence and the direction of these discontinuities are in agreement with theoretical predictions, the existing models overestimate the amount of the offset and cannot explain its dependence on the intralayer thickness. The presence of Si outdiffusion can be a possible explanation for this partial disagreement.

I. INTRODUCTION

The study of semiconductor heterojunctions has been a very active field for the last twenty years,[1] and has progressively devoted more and more attention to interface dipole contributions to the valence- and conduction-band offset.[2–4] The reasons for the increasing importance attributed to these contributions are their basic interest as well as their technological implications.

From a fundamental point of view, interface dipole effects have to be known in detail in order to provide a correct picture of the physical problem of the determination of the valence- and conduction-band discontinuity between two semiconductors;[5–8] on the other hand, if correctly mastered, these effects can be used to tune such lineup with continuity.[2–4] Thanks also to the advent of sophisticated growth techniques like molecular beam epitaxy (MBE), this latter aspect has already had a strong technological impact on systems like GaAs-based heterostructures. The unique transport properties of these systems, which are the main factor in determining their performance as devices, are determined precisely by the band offsets at the junctions between two different layers; the possibility of tailoring these discontinuities has disclosed the way to a new approach to microdevice design ("band-gap engineering").[9]

The recognition of the importance of the role of interface contributions to the band lineup has ultimately led to recent theoretical studies,[5–7] where the possibility is predicted of *creating* band offsets at GaAs polar homojunctions using *only* interfacial dipoles induced by a group-IV intralayer of atomic thickness. The basic idea underlying these studies was presented with a simple model by Harrison. In the spirit of his "theoretical alchemy" approach,[8] a Ge double layer in bulk GaAs can be imagined to be obtained by "transferring" protons from a layer of As to an adjacent layer of Ga atoms; such a charge transfer produces a microscopic planar capacitor which creates an interface electrostatic dipole on an atomic scale, inducing a band offset at the junction.

Using more sophisticated self-consistent-field[6] or linear-response-theory (LRT) calculations,[5] offsets of the order of 1 eV have been predicted for GaAs homojunctions with a Ge double layer grown along the (100) direction. A more detailed LRT study of GaAs homojunctions also explored other configurations,[7] changing the thickness (from 0 to 2 monolayers) of both Ge and Si intralayers and obtaining in this way a continuous variation of the calculated band offset (from 0 to 1.4 eV).

For the reasons mentioned above, these theoretical predictions present a strong fundamental interest and intriguing technological implications, and required therefore an immediate experimental test. In this work, we present the results of a photoemission study of MBE-grown GaAs(100) homojunctions, which provide experimental evidence that band offsets can actually be created by Si intralayers of atomic thickness using *only* interface specific contributions. Si was chosen because it is expected to produce stronger effects with respect to Ge;[7] the two intralayer thicknesses we studied (1 and 1.5 monolayers) were expected to produce band offsets large enough to be easily detectable (0.75 and 1.1 eV, respectively) and different enough from each other to be easily distinguishable.[7]

II. EXPERIMENTAL DETAILS

GaAs homojunctions and GaAs crystals were grown in a twin MBE and chemical beam epitaxy (CBE) system, and passivated with a thick As cap to protect the samples during the transfer to the photoemission chamber. GaAs crystals were grown along the (100) direction following the usual MBE prescriptions, keeping the substrate at a

temperature $T_s = 620$ °C. In order to obtain the As protective layer, the crystals were transferred to the CBE growth chamber under ultrahigh vacuum and exposed to an As_2 flux for 2.5 hours with $T_s = 0$ °C. As_2 was obtained from the AsH_3 cracker cell of the CBE chamber, and was used because of its more efficient sticking with respect to the As_4 source that was available in the MBE chamber.

The homojunctions with Si intralayers were prepared by first growing a 1-μm-thick layer of undoped GaAs, under the same conditions described above. The growth was then interrupted for approximately 1–2 minutes to cool the substrate temperature down to 500 °C. The Si intralayer was then deposited on the 2×4 As-stabilized surface, keeping the As_4 flux on. A classical Knudsen cell used for *n*-type doping was used as a Si source. It was calibrated in the range 1300–1400 K corresponding to doping levels from 1×10^{17} to 3×10^{18} cm^{-3} for growth rates of 1 μm/h; the calibration curve was then extrapolated up to 1500 K. The completion of one monolayer required 10 minutes with a Si flux of 1×10^{12} cm^{-2} s^{-1}, and produced reflection high-energy electron diffraction (RHEED) patterns consistent with the 3×1 reconstruction previously observed in the same growth conditions.[10] After the Si intralayer was deposited, the temperature was raised again and a 15–20-Å-thick GaAs layer was grown [Fig. 1(a)]. Finally, the As protective cap was deposited.

The samples were then transferred to a photoemission system, where the As cap was removed by heating. The base pressure in the experimental chamber was 1×10^{-10} Torr or better. Photoelectrons were excited by photons dispersed by the Grasshopper Mark V monochromator of the Synchrotron Radiation Center of the University of Wisconsin, and collected in angle-integrated mode by a double-pass cylindrical mirror analyzer. The overall energy resolution was 150–200 meV in the range of photon energies used in this experiment.

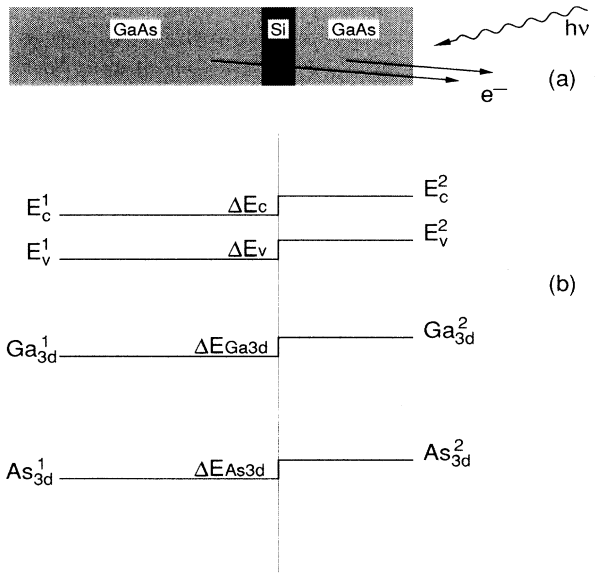

FIG. 1. (a) Sketch of GaAs homojunctions. Ultrathin Si intralayers were deposited on the As terminated surface of a 1-μm GaAs(100) substrate; a 15–20-Å-thick GaAs overlayer was then grown on top of the Si layer. (b) Schematic diagram of the energy levels at the homojunction. The valence- and conduction-band discontinuities are reflected by an offset in binding energy for the As 3*d* and Ga 3*d* levels on the two sides of the junction (superscripts 1 and 2 are relative to substrate and overlayer, respectively).

III. RESULTS

Photoemission is an established technique for the study of heterojunctions.[11] The band offset at the junction between two semiconductors can be determined by following the behavior of their photoemission features, since band bending produces a rigid shift of all the energy levels of the materials on the two sides of the junction.

For the systems we studied, GaAs with Si intralayers, we focused our attention on the Ga 3*d* and As 3*d* core levels. The way the band offset can be evaluated is illustrated in Fig. 1(b): the difference in binding energy between the core levels on the two sides reproduces the valence-band discontinuity. It is noteworthy that, if no other phenomena (like chemical reactions) occur, *both* the As 3*d* and the Ga 3*d* levels must present an offset equal to the valence-band discontinuity: $\Delta E_V = \Delta E_{As\,3d} = \Delta E_{Ga\,3d}$. Conversely, if $\Delta E_{As\,3d} = \Delta E_{Ga\,3d}$, this indicates the existence of a valence-band discontinuity equal to the core levels offset. This is especially true in our case (where the only possible chemical reactions would take place with Si), because Ga-Si reacted species show core-level energy shifts in *opposite* directions with respect to As-Si ones.[12]

Of course, for the particular case of a homojunction, it is not easy to discriminate between the overlayer and substrate contribution to the overall signal that is detected. One possible way of doing this is to probe portions of the sample with different thickness. This can be accomplished simply by varying the photon energy and consequently the photoelectron escape depth λ: specifically, the contribution of the substrate component will increase with λ. Exploiting the tunability of synchrotron radiation, we were able to vary the escape depth from 5–6 Å to about 20 Å.[13] Since the thickness of the overlayers in our homojunctions was 15–20 Å, this difference in λ is reflected by a variation in the ratio between substrate yield and overlayer yield, which goes from almost zero ($\lambda = 6$ Å) to about one ($\lambda = 20$ Å).

A least-squares-fitting procedure was used to resolve different contributions to the detected core-level intensities; the analytical expression used for each component was a doublet of Voigt functions. The parameters characterizing these functions were determined studying the As-capped GaAs(100) crystals: the protective cap was removed at 350 °C to study the As-rich surface that was in this way obtained.[14] The results are reported in Table I and in Fig. 2. They are in nice agreement with previous studies on GaAs(100) surfaces.[14]

GaAs-Si-GaAs homojunctions (with 1- and 1.5-monolayers-thick Si intralayers) were decapped in the photoemission chamber following the same procedure

TABLE I. Fitting parameters for Ga 3*d* and As 3*d* core-level spectra taken on As-rich GaAs(100)-(4×4). All energies are expressed in eV.

Parameter	Ga 3*d*	As 3*d*
Spin-orbit splitting	0.45	0.69
Branching ratio	1.61	1.56
Gaussian width	0.36	0.55
Lorentzian width	0.15	0.17
BE shift *S*1	−0.35	−0.61
BE shift *S*2	0.31	0.44

used for the GaAs crystals. As 3*d* spectra were taken at photon energies of 95, 57, and 52 eV, and Ga 3*d* at 72, 40, and 33 eV. In Table II the escape depth is shown for each case.[13] The intensity of the substrate yield relative to that of the overlayer is also given, assuming that the intensity of the detected signal decreases exponentially (with a decay length equal to λ) with the depth of the emitting atoms.

The experimental results are shown in Figs. 3 and 4. The curve-fitting procedure was performed under strict conditions: the values obtained from the GaAs(100) surfaces for branching ratios, spin-orbit splittings, surface shifts, and natural linewidths were used as fixed parameters in all the following deconvolutions. The Gaussian width was allowed to vary to match the changes in instrumental resolution at different photon energies. Since we had to take into account the existence of the substrate, one additional component was introduced, with the same line-shape parameters.

Before looking into the details, we would like to point out the evident similarity of the behavior of the Ga 3*d* and As 3*d* core levels. For both of them the additional component introduced (dashed line in Figs. 3 and 4) is more bound with respect to the bulk feature (dotted line), and for both of them the surface components (dashed-dotted line) vanish and the new component grows while increasing λ. A more detailed analysis shows that for the 1 ML (Si) case the energy shift between dashed and dotted components is about 0.3 eV for *both* Ga 3*d* and As

TABLE II. Variation of the photoelectron escape depth λ and relative intensity of I_1 (substrate yield) respect to I_2 (yield from a 15-Å-thick overlayer) for Ga 3*d* and As 3*d* core levels at different photon energies.

	Ga 3*d*			As 3*d*	
$h\nu$ (eV)	λ (Å)	I_1/I_2	$h\nu$ (eV)	λ (Å)	I_1/I_2
72	6	0.80	95	6	0.08
40	12	0.4	57	18	0.7
33	20	0.9	51	25	1.2

3*d*, and stays remarkably constant in energy [±0.03 eV, which is less than the experimental error of 0.05 eV (Ref. 1)] when varying the escape depth. The same considerations hold also for the sample with the 1.5 ML (Si) intralayer, with the difference that the energy shift is 0.25 eV. Furthermore, if one compares the relative dashed or dotted component intensity for *both* As 3*d* and Ga 3*d* with the relative substrate or overlayer yield at the corresponding λ's given in Table II, a good agreement for the corresponding ratios can be found. It is therefore immediate to assign the dotted As 3*d* and Ga 3*d* components to the overlayer and the dashed ones to the substrate. Once this association is made, it is immediately clear that these results are fully consistent with the situation shown in Fig. 1 and representing a band discontinuity between the two sides of the junction: thus, the offset between the overlayer and substrate core levels (which is, within the experimental error, the same for As 3*d* and Ga 3*d*) reflects a valence-band offset of 0.3±0.05 and 0.25±0.05 eV, respectively, for GaAs homojunctions with 1- and 1.5-ML-thick Si intralayers, with the energy levels more bound on the substrate side of the junction.

A more careful analysis is required at this point, to prove that the presence of chemically reacted species does not perturb the evaluation of the offset. The study

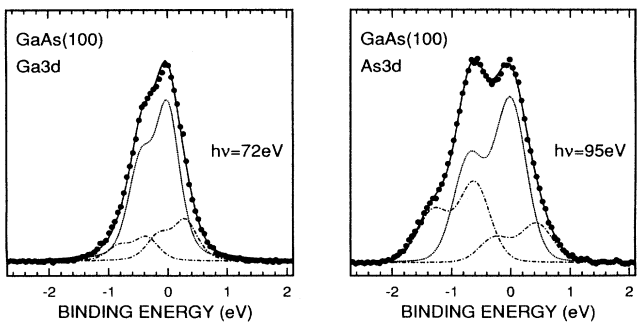

FIG. 2. As 3*d* and Ga 3*d* core levels for the As-rich GaAs(100)-(4×4) surface, showing different contributions to the overall detected signal: from the bulk (dotted line) and from the surface (dash-dotted line). The solid line is the sum of these contributions and fits very well the background-subtracted experimental points (solid circles).

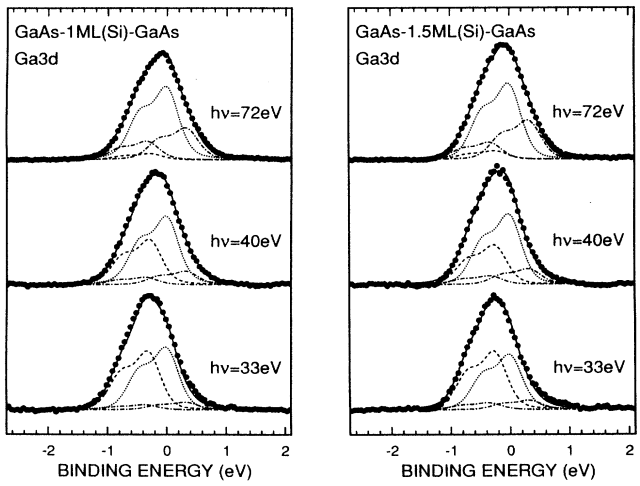

FIG. 3. Ga 3*d* core levels for GaAs homojunctions, with different levels of surface sensitivity. The dotted, dashed, and dash-dotted components represent overlayer, substrate, and surface contributions, respectively. Again, the solid circles are the experimental data after background subtraction and the solid lines are the sum of the different components.

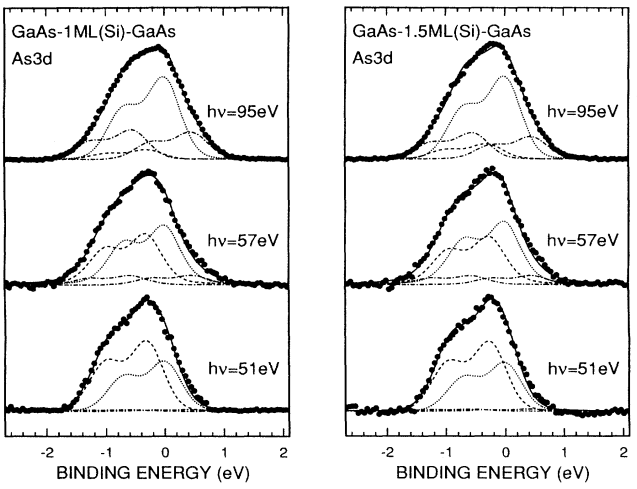

FIG. 4. As 3*d* core levels for homojunctions. The various components are represented as in Fig. 3.

of the Si 2*p* features shows that, even though most of the Si remains localized at the junction, some outdiffusion is present. This creates Si-Ga and Si-As bonds even away from the interface, and these bonds might bring their own contribution to the overall As 3*d* and Ga 3*d* signal. Simple considerations based on differences in electronegativity between Ga, Si, and As (1.13, 1.41, and 1.57, respectively)[15] and their correlation to core-level shifts[12] show that the As-Si bond should be represented by an As 3*d* feature more bound by about 0.25 eV with respect to the GaAs As 3*d* level, and similarly that the presence of Ga-Si bonds should be detected as a feature less bound by about 0.35 eV with respect to the GaAs Ga 3*d*. Consequently, the core-level shifts for these reacted forms would be very similar to those for the As 3*d* substrate component and Ga 3*d* surface state, respectively. The Ga 3*d* surface component plays no role in our evaluation of the band offset, so we will pay little attention to its double origin. As far as the As 3*d* substrate component is concerned, very simple considerations prove that the contribution the As-Si reacted forms is negligible; in fact, if such contribution were significant, the position of the dashed component should be the same, whereas its height should increase by approximately a factor 1.5 going from the 1 ML to the 1.5 ML (Si) case. The experimental results show instead the same intensity of the dashed component in the two cases, and a different position in energy, which proves that the contribution from the substrate overshadows the reacted form. Therefore possible perturbing effects in the determination of the band offset (like displacement of the centroid of the dashed component due to the presence of a feature with binding energy similar, but not perfectly equal, to the real substrate component) are negligible and can be included in the experimental error.

IV. DISCUSSION

The theoretical models[5–7] that studied band discontinuities at GaAs polar homojunctions due to group-IV intralayers predict offsets of the order of 1 eV (with the anion side of the junction more bound), always assuming that it is possible to grow such an intralayer between a cation plane on one side and an anion plane on the other. Translated to our case, this means assuming that the overlayer is Ga initiated, since the substrate is As terminated. Such an assumption must be made *cum grano salis:* the nature of the overlayer growth is actually cation initiated in the absence of Si, but one cannot rule out that it might be to some extent perturbed when the intralayer is present.[16] However, even if some caution in their application is required, these theoretical models can explain the existence and direction of the offset, because in our case the energy levels on the anion terminated side of the junction are actually more bound than on the other.

According to Peressi *et al.*,[7] valence-band offsets of 0.75 and 1.1 eV should be found for GaAs homojunctions with Si intralayers of 1 and 1.5 ML thickness, respectively. Comparable values can be extrapolated from other theoretical works, where the similar system GaAs-Ge-GaAs was considered.[5,6] The discrepancy between these calculations and our results is twofold: first, the measured discontinuities are considerably smaller than the theoretical ones; second, the band offset slightly decreases while going from 1-ML to 1.5-ML-thick Si intralayers, instead of increasing as predicted in Ref. 7.

This quantitative disagreement confirms what was already found when the same computational methods were used to study similar systems, like III-V/III-V heterojunctions with group-IV intralayers[16,17] or group-IV homojunctions with III-V double intralayers:[18–20] the maximum valence-band offset (that never exceeds a critical value of about 0.4–0.5 eV), is considerably smaller than the predicted discontinuities, no matter what the thickness is of the group-IV intralayer at GaAs-AlAs heterojunctions[16,17] or the number of III-V double layers at Si homojunctions.[20]

The partial interdiffusion of the Si intralayer, that several studies on δ doping of GaAs have thoroughly explored,[21] is one of the effects that can explain both aspects of such disagreement with the theoretical models (migration of Si in GaAs lessens the interface dipole,[7] and becomes more relevant when the intralayer thickness is increased). Other interpretations, proposed for GaAs-AlAs heterojunctions and related to cation-anion swaps driven by the strong electrostatic field at the interface,[17] can be also considered. These swaps, obviously, need not exclude Si interdiffusion; in our opinion these effects are instead likely to be simultaneously present. The unsatisfactory agreement with theory is therefore attributed to migration across the interface of all the chemical species that are present; such migration causes a charge redistribution different from the one expected for the ideally abrupt configuration, and requires new and more refined models to predict the interface dipole.

V. CONCLUSION

In conclusion, the theoretically predicted possibility of creating tunable band offsets at GaAs polar homojunctions using group-IV intralayers of variable atomic thick-

ness has been successfully verified for the specific case GaAs-Si-GaAs(100). This confirms that it is possible to use interface electrostatic dipoles not only to modify a preexisting offset, but also to produce discontinuities of potential technological interest at junctions that would otherwise present perfectly aligned bands. Current theories tend nevertheless to overestimate the amount of these discontinuities, especially for thicker Si intralayers. New models that take into account the presence of Si diffusion are in our opinion necessary to provide a more realistic description of these systems.

ACKNOWLEDGMENTS

This work was supported by the Fonds National Suisse de la Recherche Scientifique, by the National Science Foundation, and by the Ecole Polytechnique Fédérale de Lausanne. One of the authors (M.M) acknowledges financial aid from Fondazione Angelo della Riccia. The Synchrotron Radiation Center of the University of Wisconsin is a national facility supported by the National Science Foundation (NSF).

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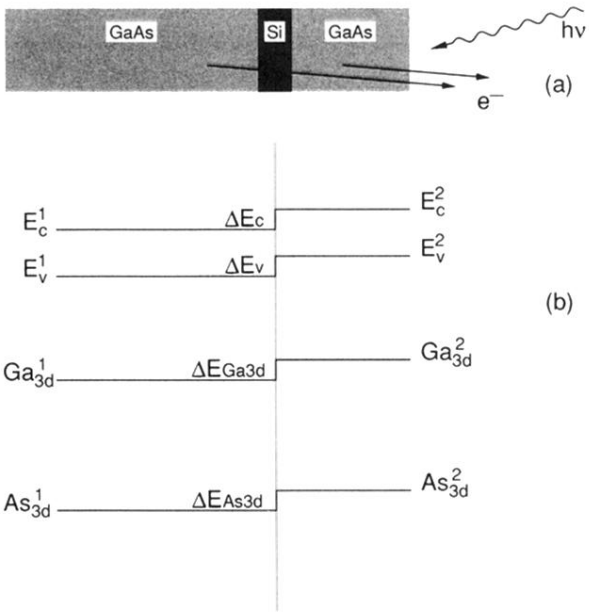

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