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Tuning band offsets at semiconductor interfaces by intralayer deposition

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Band offsets can be modified at semiconductor heterojunctions or created at homojunctions by depositing thin intralayers of group-IV atoms at III-V/III-V polar interfaces. We present here a theoretical study of Si and Ge intralayers deposited along (001) at GaAs and AlAs homojunctions, and at GaAs/AlAs heterojunctions. Our results show that the offset is very sensitive to the coverage and abruptness of the intralayer. A comparison with recent experiments for Si in GaAs/AlAs suggests that Si atoms are confined over two atomic planes for coverages lower than about 0.5 monolayers, whereas for higher coverages Si diffusion occurs.

Band offsets at semiconductor heterojunctions are fundamental parameters which govern the transport properties of microelectronic devices. Tuning them is therefore a great scientific and technological challenge.[1] Existing experimental data suggest and recent theoretical work confirms that—at isovalent heterojunctions—the band offsets depend only on the bulk properties of the two constituents.[2–4] In particular, they are independent of the orientation and of the quality of the interface.[4] At polar interfaces between heterovalent semiconductors the offsets depend instead on the microscopic details of the interface.[4–8] These systems are therefore ideal candidates as *tunable* heterojunctions.[4,8] Controlling and modifying the band discontinuities even at isovalent heterojunctions such as GaAs/AlAs would be of great practical interest and would open up broad perspectives in the field of band-gap engineering. One of the possible ways of modifying the intrinsic interface dipole at an isovalent interface is to introduce a double layer of atoms with different chemical valence, which would then act as a microscopic capacitor.[4,9] We indicate this kind of extremely localized δ doping by the term "δ' doping." δ' doping is an evolution of the doping interface dipole (DID) introduced by Capasso and co-workers,[10] in that it corresponds to higher doping concentrations, and a length scale down to the extreme atomic limit. According to Harrison's model,[5] a double layer of (say) Ge in GaAs can be thought of as arising from the transfer of protons from an As layer to an adjacent Ga layer, thus producing a dipole sheet in bulk GaAs, whose magnitude is then reduced by electronic screening. More recently, a general theory of band offsets—based on linear-response-theory (LRT) concepts—has been proposed,[4] which puts Harrison's model on a firm theoretical basis. Self-consistent-field (SCF) calculations have quantitatively confirmed the possibility of creating a potential drop across a δ' bilayer in an otherwise perfect semiconductor.[9] The actual realization of δ' doping has long been considered unfeasible, due to atomic interdiffusion which would hinder the sharp localization of dopants. Only very recently, it has been demonstrated that in the case of Ge/GaAs/Ge (111) (Ref. 11) and GaAs/Si/AlAs (001) (Ref. 12) δ' doping can indeed be realized, and the corresponding modifications of the band offsets have been measured.

In the present work we study the effects of Ge and Si (001) intralayers inserted in bulk GaAs and AlAs crystals (intralayers at homojunctions), and at GaAs/AlAs heterojunctions. We start with a brief discussion of our theoretical techniques (supercell SCF calculations and LRT approach); we then present our results for Ge intralayers at GaAs and AlAs homojunctions, and at GaAs/AlAs heterojunctions; finally, we discuss our results for Si intralayers at GaAs/AlAs heterojunctions in conjunction with recent experimental data.[12]

As usual, we split the valence-band offset (VBO) into an electrostatic contribution—the potential lineup ΔV—and a band contribution, ΔE_v.[4] We focus here our attention on the former, because the latter is by definition a bulk property of the two constituents, which cannot therefore depend on any structural detail of the interface: in particular, it vanishes in the case of homojunctions. The potential lineup can be obtained from SCF calculations, or through the LRT approach of Ref. 4.

SCF calculations are performed within density-functional theory, using the local-density approximation (LDA), norm-conserving pseudopotentials, and plane-wave (PW) basis sets up to a kinetic-energy cutoff of 8 Ry. Isolated interfaces have been simulated using periodically repeated supercells containing 16 atoms; Brillouin-zone (BZ) integrations have been performed using a set

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of special points which corresponds to 10 points in the irreducible wedge of the zinc-blende BZ.

We recall now the main points of our LRT approach[4] which are relevant to the present situation. The interface A/B between two semiconductors, A and B, is treated as a *perturbation* with respect to a properly chosen periodic reference (virtual) crystal $\langle AB \rangle$: the bare potential describing such a perturbation is the sum of localized potentials which transform the virtual ions into real ones. The electrostatic-potential lineup across the interface is obtained to linear order from the charge-density response to these localized perturbations. It can be shown that for isovalent interfaces such as GaAs/AlAs—where such perturbations are neutral—the band offset is to linear order a bulk property of the two constituents, independent of the structural details of the interface. In the case of heterovalent heterojunctions such as Ge/GaAs, the localized bare perturbations are no longer neutral, and the response can be split into two contributions: the first, which we call $\Delta V^{(2)}$, is similar to the isovalent case, and it is therefore independent of interface details; the second contribution ($\Delta V^{(0)}$) depends instead on such details, but, to linear order in the perturbation, it can be easily calculated once these are known. In fact, $\Delta V^{(0)}$ is equal to the electrostatic-potential lineup generated by an assembly of classical point charges $\Delta Z_i/\epsilon_\infty$, where ΔZ_i is the bare charge carried by the perturbation at the ith site, and ϵ_∞ is the static dielectric constant of the virtual crystal.

In order to display the mechanism which allows one to tune the band offset at polar interfaces, let us consider the case of Ge/GaAs (001).[7] Two inequivalent cases are possible, according to whether GaAs is Ga- or As-terminated. The $\Delta V^{(2)}$ terms are the same in the two cases, whereas the $\Delta V^{(0)}$'s have opposite signs, thus giving rise to different total lineups. Heterovalent intralayers at polar III-V interfaces can be treated along similar lines. Consider, e.g., the case of GaAs, where a full (001) bilayer is substituted with Ge: we thus get a GaAs/Ge/GaAs (001) homojunction. This system can be thought of as built in two steps: we construct first a GaAs/Ge interface, and then a second Ge/GaAs interface shifted by two layers with respect to the first. The VBO across the Ge bilayer is then the difference between the lineups of the two (inequivalent) interfaces.

We have performed SCF calculations for this homojunction at different dopant coverages, x (x=2 corresponds to the bilayer considered above). In order to ensure local charge neutrality—which is required by thermodynamical stability—Ge atoms have to be spread over at least two atomic layers, even at coverages $x<2$. In the absence of any information about the actual atomic arrangement of dopants, we assume that Ge dopants are uniformly distributed over two consecutive atomic layers, for any coverage; virtual ions $\langle Ga_{1-x/2}Ge_{x/2} \rangle$ and $\langle As_{1-x/2}Ge_{x/2} \rangle$ are used to describe the δ' bilayer for $x \neq 2$. Lattice relaxation possibly occurring at the interface is neglected for the time being. In Fig. 1 we

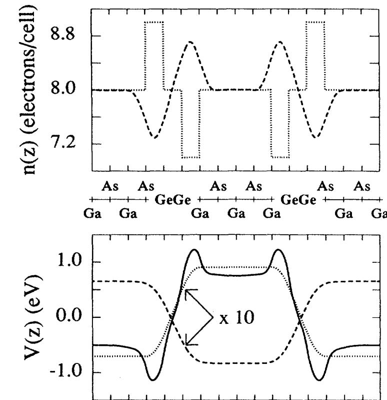

FIG. 1. Macroscopic averages of the electronic (dashed lines) and nuclear (dotted lines) charge densities and electrostatic potentials of a Ge bilayer in GaAs. In the latter case, the scale refers to the total potential (solid line), whereas the electronic and nuclear contributions are scaled by a factor 10.

display the macroscopic averages[4] of the nuclear- and electronic-charge-density distributions and electrostatic potentials, corresponding to x=2. For a general coverage, the nuclear contribution to the lineup is easily calculated to be $\Delta V^n = (\pi e^2/a)x$, where a is the equilibrium lattice constant of GaAs; at x=2 this gives $\Delta V^n = +16.09$ eV. SCF calculations provide the electronic contribution $\Delta V^e_{SCF} = -14.87$ eV, which has an opposite sign and a similar magnitude: the resulting offset is $\Delta V_{SCF} = \Delta V^e_{SCF} + \Delta V^n = +1.22$ eV, the As-terminated portion of GaAs being lower in energy. We note that only the electronic contribution is subject to numerical inaccuracies; however, due to substantial cancellation, the total lineup is rather sensitive to these inaccuracies. We estimate the absolute accuracy of ΔV^e_{SCF} to be of the order of 0.1 eV (due to the incompleteness of our PW basis

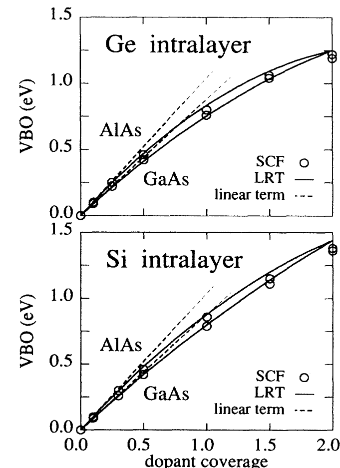

FIG. 2. VBO at GaAs and AlAs homojunctions as functions of the coverage of a Ge or Si intralayer. SCF results are indicated by circles; the solid lines correspond to the predictions of Eq. (1); the dashed lines indicate the linear behavior predicted by Eq. (1) at small coverages.

sets, approximate BZ sampling, and so on), resulting in a relative accuracy of $\sim 10\%$ in the final result.

In the upper panel of Fig. 2 we report the VBO for GaAs/Ge/GaAs and for AlAs/Ge/AlAs, as provided by several SCF calculations at different coverages (circles). The x dependence of the offset shows a substantial bowing, while the LRT of Ref. 4 would predict the simple linear behavior $\Delta V \approx (\pi e^2/a\epsilon_\infty)x$—where ϵ_∞ is the host dielectric constant—when the host is treated as the reference (unperturbed) system. Inspection of the data shows indeed that the linear behavior (dashed lines) is closely obeyed at low coverages.

The deviation from linearity can be understood in terms of elementary electrostatics. The δ' bilayer acts as a microscopic capacitor whose plates are one interplanar spacing apart, and whose charge and capacitance are determined—through macroscopic electrostatics—by the concentration of dopants. In this capacitor, the effective inverse dielectric constant is that of an hypothetical bulk alloy, with the same composition as the doped bilayer: $\epsilon_\infty^{-1}(x) = (1 - x/2)\epsilon_h^{-1} + (x/2)\epsilon_i^{-1}$, where ϵ_h (ϵ_i) is the host (dopant) dielectric constant. The final result reads

$$\Delta V(x) = \frac{\pi e^2 x}{a\epsilon_\infty(x)} = \frac{\pi e^2 x}{a}\left(\epsilon_h^{-1} + \frac{x}{2}(\epsilon_i^{-1} - \epsilon_h^{-1})\right). \quad (1)$$

Equation (1) can be derived from LRT by considering the alloy as the (unperturbed) reference system, and the difference between the real system and this alloy as the perturbation. As the electric field responsible for the potential lineup practically vanishes one atomic plane apart from the doped bilayer (see Fig. 1), this choice for the (arbitrary) reference system results to be optimal.

According to Eq. (1), the linear behavior of the VBO corresponding to small concentrations of Ge is different for GaAs and AlAs homojunctions, because of the different dielectric constants of the two hosts, whereas the VBO is the same for x=2. Following Eq. (1) again for Si intralayers (lower panel of Fig. 2), the linear behavior of the VBO corresponding to small doping is the same as for Ge intralayers, being dominated by the electrostatic screening of the hosts. At high coverage, and in particular for x=2, the VBO induced by Si is higher than that induced by Ge, because of the lower dielectric constant of Si, and again equal in the two homojunctions. The excellent agreement between the predictions of Eq. (1) and SCF calculations confirms the soundness of the physical picture underlying it.

We then studied some cases where the dopants are not confined within a bilayer. When the dopant concentration does not vary over pairs of adjacent cationic and anionic planes (i.e., when the situation can be described by a series of microscopic capacitors), Eq. (1) can be easily generalized and predicts an increasing magnitude of the VBO whenever the dopant concentration decreases from the first two layers on. Sample SCF calculations confirm the validity of this generalization.

We come now to the case where a Ge or Si intralayer is deposited at a (001) interface between GaAs and AlAs. We have to distinguish two inequivalent situations, according to whether GaAs is cation- or anion-terminated. Due to the larger stability of As-terminated (001) surfaces, the two situations correspond to AlAs/X/GaAs and GaAs/X/AlAs growth sequences respectively (X =Ge,Si). The total band offset is the sum of the intrinsic VBO at the GaAs/AlAs interface (which of course changes its sign by inverting the growth sequence), plus the local dipole induced by the intralayer: VBO(GaAs/X/AlAs)$\approx$ VBO(GaAs/AlAs)+$\Delta V_{\rm intra}$ and VBO(AlAs/X/GaAs)$\approx$ $-$VBO(GaAs/AlAs)+$\Delta V_{\rm intra}$. In Fig. 3 we report the VBO at the GaAs/AlAs (001) interface, as a function of the coverage of a Si intralayer (circles), calculated neglecting lattice relaxation (i.e., assuming that all the atoms stay at their ideal zinc-blende lattice sites). Also in this case, Eq. (1) accurately predicts the results of SCF calculations.[13]

Our results compare rather well with experiments[12] (squares) up to a coverage $x \approx 0.5$, whereas a substantial discrepancy appears for higher coverages. To assess whether this discrepancy is due to neglecting lattice relaxation at the interface, we have undertaken a series of SCF calculations aimed at optimizing the atomic positions in our supercell and estimating the effect on the VBO. We assume that the in-plane lattice constant $a_\parallel$ is that of perfect GaAs or AlAs crystals, and optimize the total energy of the supercell as a function of c/a and of the individual atomic positions. Relaxation is studied for Si in GaAs, at x=0.5, 1, and 2; in all the above cases the microscopic strain is confined between the two doped planes and between these and the nearest neighbors. The microscopic strain is proportional to the Si coverage x within 1%, which is the uncertainty in the determination of the equilibrium interplanar distances. Linear interpolation of our results gives $u_{\text{Si-As}}(x) \approx +0.004ax$, $u_{\text{Si-Ga}}(x) \approx -0.004ax$, and $u_{\text{Si-Si}}(x) \approx -0.012ax$, where u is the variation of the interplanar spacing. Test calcu-

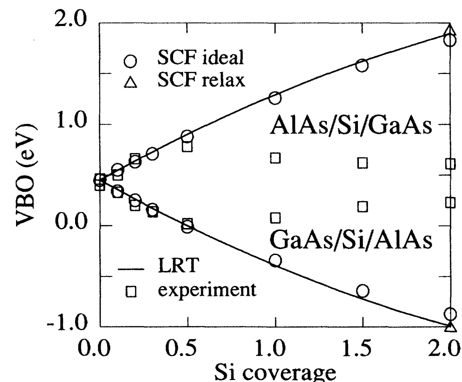

FIG. 3. VBO at GaAs/AlAs heterojunctions as a function of the coverage of a Si intralayer. Circles: supercell SCF results for the ideal unrelaxed structures. Triangles: supercell SCF results including microscopic relaxation. Squares: experimental data from Ref. 12. Solid lines: present theory predictions of Eq. (1).

lations performed for AlAs/Si/AlAs, GaAs/Si/AlAs, and AlAs/Si/GaAs at x=2 show that similar results hold for all these cases. By studying separately Si-As, Si-Ga, and Si-Si strains we have estimated that their effects on the VBO, $\Delta V_{\rm strain}$, are separately smaller than 0.06 eV, and that the first two tend to cancel each other; the final estimate of $\Delta V_{\rm strain}$ when full relaxation is considered is smaller than 0.1 eV at x=2 (see Fig. 3). Microscopic strain tends to increase rather than to reduce the VBO, and its effects are anyhow much smaller than the disagreement between theory and experiments.

In our opinion the comparison between experimental results and theoretical predictions suggests that in real samples Si dopants stay indeed confined in one bilayer for coverages $x < 0.5$, and that the departure of the measured VBO from theoretical predictions at higher coverages can be attributed to Si diffusion.

Due to the greater stability of As-terminated (001) surfaces, it is reasonable to assume that the first-deposited Si atoms stick at cationic sites. For the same reason, dopant diffusion should preferably affect planes grown after the Si deposition. As we have seen before, Si diffusion tends to increase the magnitude of the intralayer contribution to the VBO, when the dopant concentration does not vary over pairs of adjacent atomic planes. Equation (1) cannot be easily extended to an arbitrary density profile because, in the general case, it may be difficult to find an optimal reference system for LRT. However, starting from *any* reasonable reference system, LRT suggests—and sample SCF calculations confirm—that the above conclusions on the increase of the lineup can be generalized to those cases where the dopant concentration decreases in the first deposited layers, provided no antisites are produced. We conclude that only the presence of antisites can determine the decrease of the offset observed for x>0.5. Assuming our hypothesis that at lower coverages Si atoms stay confined on two layers, the findings seem to indicate that around a critical alloy concentration—namely $(GaAs)_{0.75}(Si_2)_{0.25}$—the zinc-blende order tends to be lost during epitaxial growth. This fact suggests a relation (which may be accidental) with the critical composition at which III-V–IV alloys undergo an order-disorder transition from the zinc-blende to the diamond structure.[14]

According to our previous analysis, the calculated VBO's crucially depend on the values of the dielectric constant used. We observe that LDA tends to overestimate the dielectric constants by ~10%, while our rather small PW basis set tends to reduce them. The two effects partially cancel each other, the resulting values of ϵ being smaller than experiment.[15] In order to check Eq. (1) against benchmark SCF calculations, such theoretical values have been consistently used here. Once the soundness of the physical picture underlying Eq. (1) has been so assessed, Eq. (1) should be better if used with experimental dielectric constants, but this would not alter the conclusions of the present paper.

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[13] The value of the host dielectric constant used in this case is the average between the theoretical dielectric constants of AlAs and GaAs: $\epsilon_h^{-1} = \epsilon_{\rm GaAs}^{-1} + \epsilon_{\rm AlAs}^{-1}$.

[14] For $Ge_x(GaSb)_{1-x/2}$, for instance, an order-disorder transition is observed at $x_c \sim 0.5$. See, e.g., E.A. Stern, F. Ellis, K. Kim, L. Romano, S.I. Shah, and J.E. Greene, Phys. Rev. Lett. **54**, 905 (1985).

[15] The dielectric constants calculated with the same kinetic energy cutoff and an equivalent number of special points as used here are 9.2, 7.7, 12.8, and 10.8 for GaAs, AlAs, Ge, and Si, while the experimental values are 10.9, 8.2, 15.4, and 11.4, respectively.