

Heterojunction band offsets for polar interfaces: From a thin to a thick covalent intralayer

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A self-consistent linear combination of atomic orbitals method is used to calculate the band offsets for the ideal GaAs/Ge/GaAs-(100) and GaAs/Ge/AlAs-(100) interfaces, both for a few Ge monolayers and for a thick Ge intralayer. This thick limit is deduced using the results for the cation- and anion-terminated ideal GaAs/Ge- and AlAs/Ge-(100) interfaces. Charge transfer and band bending at the interface region are analyzed. Our results show that the band offset increases initially with the number of Ge monolayers deposited, and saturates, approximately, at three monolayers, for which the thick intralayer limit is reached. The final band offset is mainly due to the band bendings produced by the different electronic charges accumulated in the anionlike and cationlike interfaces.

I. INTRODUCTION

Tuning heterojunction band offsets^{1,2} according to the device necessities is the dream of an advanced technology. Experimental and theoretical work in the past few years has tried to achieve and understand that tuning, using different approaches. In the mid-1980s, experimental evidence³⁻⁶ showed that in nonpolar (110) lattice-matched heterojunctions, band offsets can be modified by the deposition of a metal intralayer at the interface, and that these modifications depend on the metal electropositivity. Theoretical work,⁷⁻⁹ using a consistent linear combination of atomic orbitals (LCAO) method, showed that the basic mechanism controlling the band offsets is the alignment of the charge neutrality levels (CNL's) of the semiconductors forming the junction, and explained that the changes in the band offsets were mainly due to the modifications introduced in the CNL's of both semiconductors by the metal deposition. These results also confirmed the role of the intralayer electropositivity in the band-offset modifications.

Recently, after the work of Ref. 10, several experimental and theoretical works¹¹⁻¹³ have found important band-offset modifications using a semiconductor intralayer at a polar interface. Typical cases are the GaAs/Ge/GaAs-(100) and AlAs/Si/GaAs-(100) heterojunctions; here, both experimental and theoretical evidence has shown a strong dependence of the heterojunction band offset on the amount of the semiconductor de-

posited at the interface.

In this paper we present a theoretical analysis of the band-offset modifications introduced by a Ge intralayer between the different homointerfaces and heterointerfaces obtained with GaAs and AlAs. Recently, Peressi *et al.*¹³ have reported some theoretical results obtained using a local-density approximation for similar interfaces but considering only a covalent intralayer not larger than two monolayers. Moreover, these results were obtained by using supercells containing 16 layers; this implies that the interface is simulated with only six monolayers. In our calculations, we use a consistent LCAO method¹⁴ that has been found to yield very good results for the band offset of ideal heterojunctions.¹⁵ We calculate the different interfaces (with the intralayer included) by considering semi-infinite semiconductors, and analyze the limit of a thick intralayer by discussing separately the two ideal interfaces appearing between Ge and the ionic semiconductors. Although this thick covalent limit does not seem to be stable¹⁶ [in the sense that the energy will be lowered by substituting atoms in few interface layers to have mixed Ge-Ga and/or mixed Ge-As layers which give a compensated (neutral) interface], it is worth discussing this limit as a check to the calculations for a thin covalent intralayer.

The paper is organized as follows. In Sec. II we outline the model used to calculate the interface. In Sec. III we discuss our results, and in Sec. IV we present our conclusions.

II. THE MODEL

Figure 1 shows the geometry of a particular (100)-ionic heterojunction having a covalent intralayer. In our self-consistent LCAO method, the electronic band structure of the different semiconductors forming the interface is described by means of a tight-binding model: we follow Vogl, Hjalmarson, and Dow¹⁷ and introduce the sp^3s^* hybrids for each atom, with interactions extending up to first neighbors. In the analysis of the different interfaces presented here, we assume that the two crystals have a perfect lattice matching. Then, we define the interface Hamiltonian by taking for the interaction parameters between different crystals an average of the interactions for each semiconductor. This procedure has been shown to give very good results for the band offsets of nonpolar interfaces.^{15,7-9}

As discussed elsewhere,¹⁴ the initial Hamiltonian should be defined completely by referring the energy levels of the different semiconductors to each other by using some kind of "unperturbed" case. This is provided by the ideal cases that are defined in the following way.

(i) First, for GaAs consider the electron charge distribution for the infinite crystal. In this case, assume that the calculation of the electronic band structure yields an extra charge of 4α electrons for As and -4α electrons for Ga (these charges are measured with respect to the nuclear charges of 5 and 3 for As and Ga, respectively). This implies that α yields the transfer of charge per bond, between Ga and As. Then, if we assume to have a GaAs(100) surface, two Ga-As bonds per As are broken and the As surface layer has only 2α charges per atom. So, the initial case used in our calculation is provided by these charges, as shown in Fig. 1. Notice that the electrostatic potential associated with this charge distribution remains finite when we move inside the semi-infinite semiconductor, as expected on electrostatic stability arguments.

(ii) For AlAs a similar argument is used, and the ideal

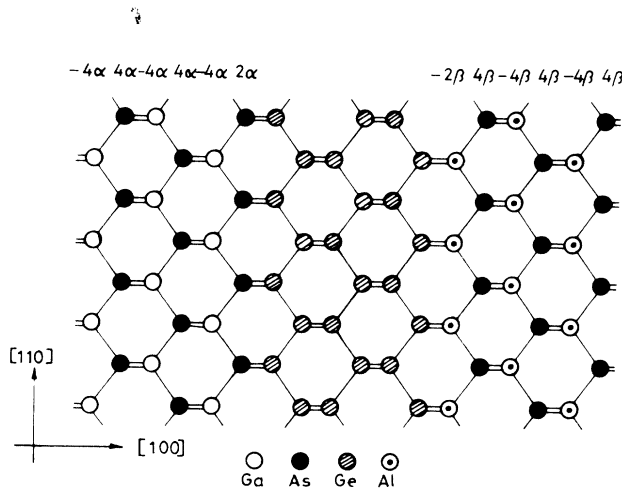


FIG. 1. GaAs/AlAs-(100) heterojunction with an intralayer formed by six Ge monolayers, showing the initial charges per atom at each layer (α is the transfer of charge per bond between Ga and As, β referring to Al and As).

charges of the initial case are also shown in Fig. 1, with 4β charges in bulk As and -2β charges in the last Al layer.

(iii) The case of Ge is trivial, since no transfer of charge between different atoms appears in the bulk.

The three previous cases define the initial charges we take as a reference for calculating the modification introduced in the electronic charge by connecting the two interfaces. The next step is to define the initial energy levels of the three crystals for the initial distribution of charges shown in Fig. 1. Our point is that those initial charges correspond to the ideal distribution of charge associated with the free surfaces of the different semiconductors: this suggests we should refer the initial electronic levels of the different crystals to each other by means of the semiconductor affinity levels.

This way of proceeding starts with an ideal case and allows for the electronic charge to readjust itself by being transferred between different crystals. As shown in previous references,¹⁴ this method yields very good results for the band offset of different (110) interfaces, the main reason being that it introduces in a self-consistent way the flow of electronic charge, as a function of the relative position of the CNL's of the semiconductor forming the interface.

In particular, the induced electrostatic potential at each layer, V_i , is related to the transfer of charge δn_i by the usual electrostatic equations.¹⁴ Here, δn_i is defined as the difference between the total charge, n_i , and the initial ones defined above. Our self-consistent calculation yields V_i by establishing that these potentials are created by the extra charges, δn_i .

Let us finally mention that once we know the interface Hamiltonian, the electronic density of states and the electron charge is obtained by using the decimation technique as described in Ref. 18. This method projects the bulk Green function of each semi-infinite crystal onto a few crystal layers at the interface, yielding an effective Green function (or, equivalently, an effective Hamiltonian) for these layers. This effective Hamiltonian is different for each energy and wave vector in the two-dimensional Brillouin zone. In this way we can define an effective Hamiltonian for the whole interface which includes only the few layers where we have projected onto the two different semi-infinite semiconductors. Typically, in our calculations we include four layers of each semiconductor, although in some cases we need to extend the number of layers up to ten, in order to get a good consistency in the problem. From this effective Hamiltonian, the electron density of states and the electron charges at the different interface layers are calculated.

III. RESULTS

Let us first consider the thick intralayer limit. Figure 2 shows the geometry of a particular interface GaAs/Ge (100), with GaAs terminated on As (we suppose to have undoped materials). The main characteristic of this interface is its polar character: for an As-terminated interface, we find that the valence bands of the two semiconductors are fully occupied, and we still have $\frac{1}{2}$ of an

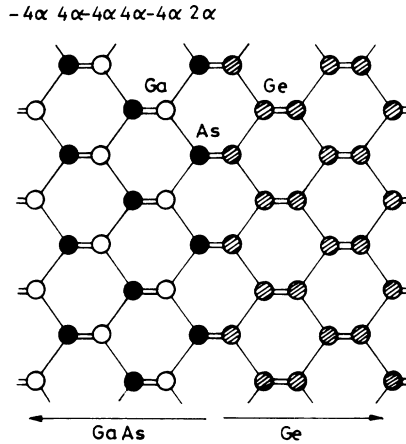


FIG. 2. GaAs/Ge-(100) heterojunction.

electron per surface atom that should be accommodated in the conduction bands. For a Ga-terminated interface, there appears $\frac{1}{2}$ of a hole per surface atom located in the valence bands.

The self-consistent equations for the interface electrostatic potential should yield an important band bending, allowing to accommodate the extra charge at the interface. Figure 3 shows the induced electrostatic potential as calculated for a GaAs/Ge-(100) heterojunction and the corresponding band bendings, for both the Ga- and the As-terminated interfaces. The Ga-terminated interface shows a large band bending with the Fermi energy coinciding practically with the Ge valence-band top; thus, an extra hole density of states is accommodated in the valence bands. The As-terminated interface shows a smaller band bending; in this case, the Fermi energy appears below the semiconductor conduction band, with the extra electron density accommodated in the interface density of states induced below the conduction-band edges. Notice, in this regard, that the As-Ge interface appears in our calculation as introducing a larger perturbation in the electron density of states than the Ga-Ge one: the As-Ge interaction creates a strong density of states below the two semiconductor conduction bands (see Fig. 4) where the extra $\frac{1}{2}$ of an electron is accommodated without having to create the strong band bending appearing in the Ga-terminated interface. Both the absence of an important density of states pulled from the valence band and the band bending are clearly seen

TABLE I. Final band offset ΔE_v and Fermi energy level E_F , both referred to the ionic semiconductor valence-band top, for the corresponding cation- and anion-terminated interfaces GaAs/Ge and AlAs/Ge (100).

	ΔE_v (eV)	E_F (eV)
GaAs/Ge-(100) Ga	0.10	0.10
GaAs/Ge-(100) As	0.75	1.30
AlAs/Ge-(100) Al	0.33	0.33
AlAs/Ge-(100) As	1.10	1.64

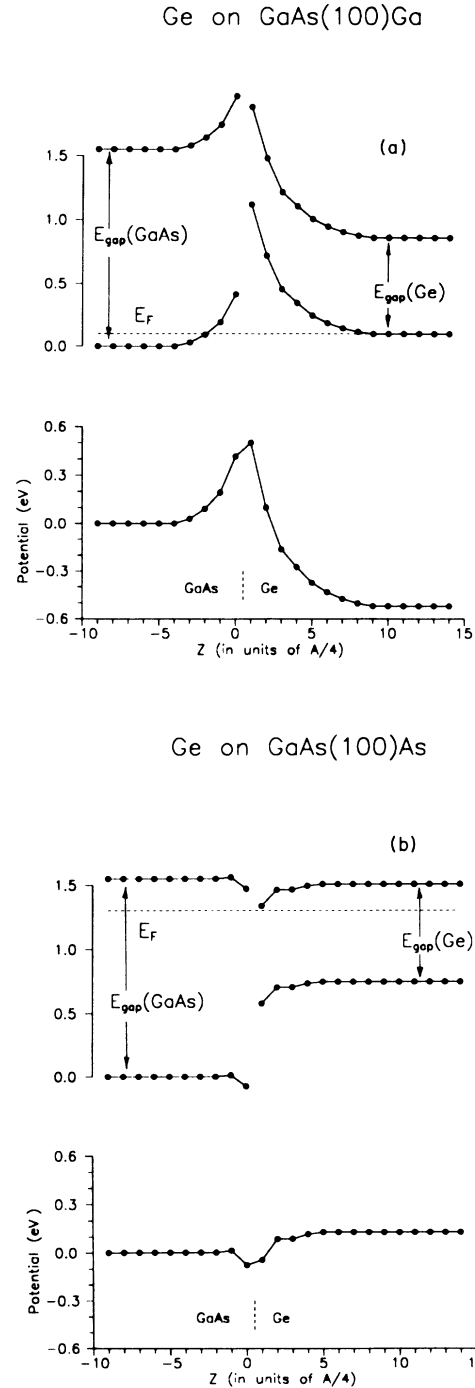


FIG. 3. (a) Electrostatic potential (bottom) and semiconductor band bending (top) (in eV) for a Ga-terminated GaAs/Ge-(100) interface (each dot represents a semiconductor layer). The separation between the curves representing the band bending is the corresponding energy gap. The Fermi level E_F is also shown. Notice the hole density that is accommodated in the valence-band. The zero of energy for the electron bands is the valence band top of the ionic semiconductor. (b) As (a) for an As-terminated GaAs/Ge-(100) interface. In this case the extra electron charge is accommodated in the density of interface states induced near the conduction-band bottom.

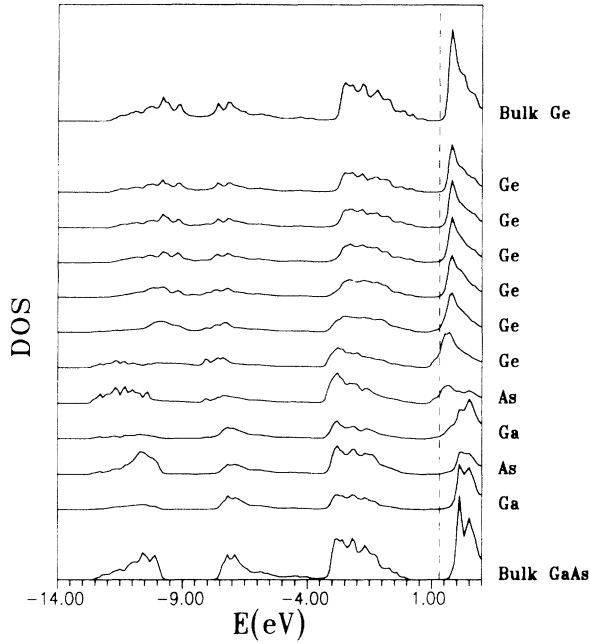


FIG. 4. Local density of states (LDOS) for each layer at the As-terminated GaAs/Ge-(100) interface. Notice the density of states created below the two semiconductor conduction bands. ($E=0$ corresponds to the GaAs valence-band top.)

in Fig. 5, where the LDOS for each layer at the Ga-terminated GaAs/Ge (100) interface is shown.

Table I summarizes the main results of Fig. 3, showing the final band offset ΔE_v for the two interfaces and the

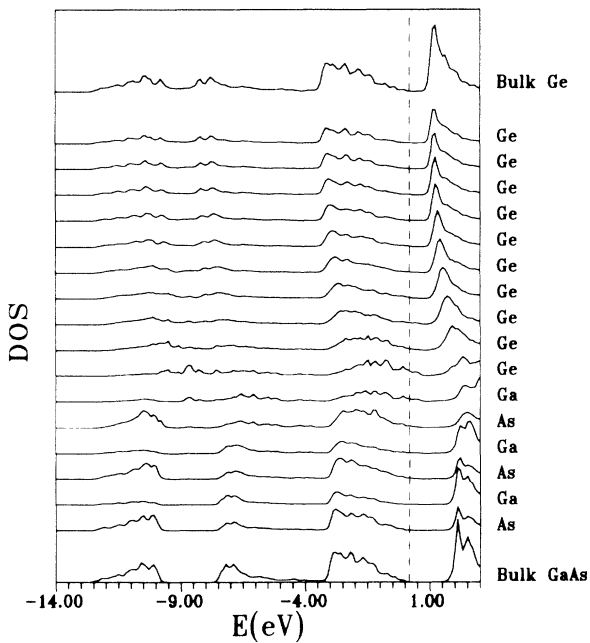


FIG. 5. Local density of states (LDOS) for each layer at the Ga-terminated GaAs/Ge-(100) interface. Notice the important band bending near the interface, especially in the Ge layers. ($E=0$ corresponds to the GaAs valence-band top.)

Fermi energy level E_F referred to the ionic semiconductor valence-band top. It is worth commenting that the band offsets, calculated for the Ga- and As-terminated interfaces, differ significantly with each other; in fact, this is due to the different band bendings appearing in both cases: the extra holes and the extra electrons induce an extra electrostatic potential, bending the bands in oppo-

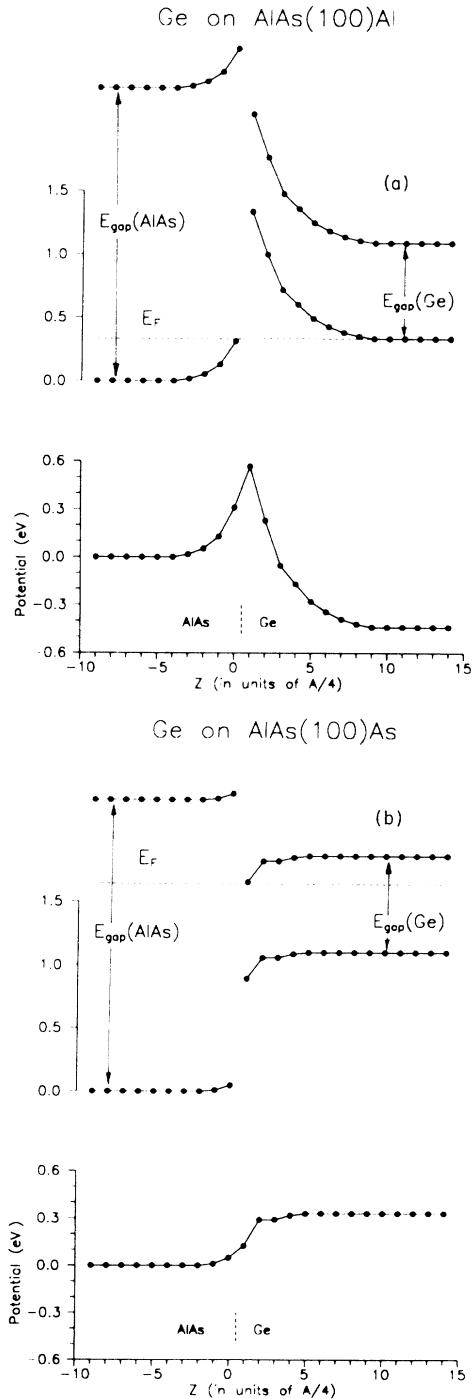


FIG. 6. (a) As in Fig. 3(a) for an Al-terminated AlAs/Ge-(100) interface. (b) As in Fig. 3(b) for an As-terminated AlAs/Ge-(100) interface.

site directions. It is of interest to see that the value of the band offset between the last layers of GaAs and Ge, for the Ga- and As-terminated interfaces, is around 0.6 eV, in good agreement with the band offset of the nonpolar heterojunction GaAs/Ge (110).¹⁵ Notice that the difference in the value of ΔE_v for the two polar heterojunctions and the (110) case is less important in the As-terminated interface because the band bending is rather small in this case.

Figure 6 shows our results for the different polar AlAs/Ge-(100) interfaces. We find for these cases similar results to the ones discussed for the GaAs/Ge-(100) heterojunctions. Table I also summarizes the main results for this interface.

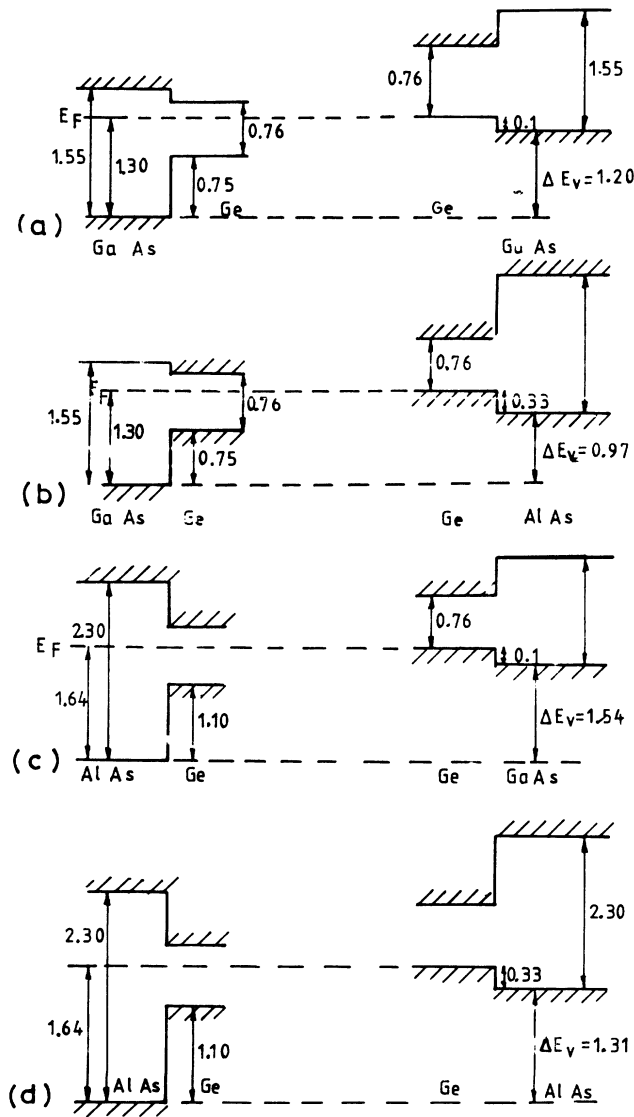


FIG. 7. Alignment of the Fermi levels and the energy gaps for a thick Ge intralayer between (a) a GaAs/GaAs-(100), (b) a GaAs(As-terminated)/AlAs-(100), (c) an AlAs(As-terminated)/GaAs-(100), and (d) an AlAs/AlAs-(100) heterojunction.

Once we have discussed the different polar heterojunctions, we turn our attention to the problem of finding the different band offset for the polar interfaces GaAs/GaAs (100), GaAs/AlAs (100), AlAs/GaAs (100), and AlAs/AlAs (100) in the limit of a very thick Ge intralayer. Figure 7 shows how the different interfaces are built up for each heterojunction. The main point to notice is that in the limit of a very thick intralayer, the two interfaces should be joined by aligning their Fermi levels; it should be commented that this implies an extra band bending in the Ge intralayer, a bending that should be created by some charge transfer from one interface to the other. Notice that for a very thick intralayer, a very small charge transfer is enough to create the electrostatic dipole aligning the Fermi levels. Then, the semiconductor bands and the energy gaps should be aligned as shown in Fig. 7. From this figure, we obtain the following band offsets for a thick Ge intralayer:

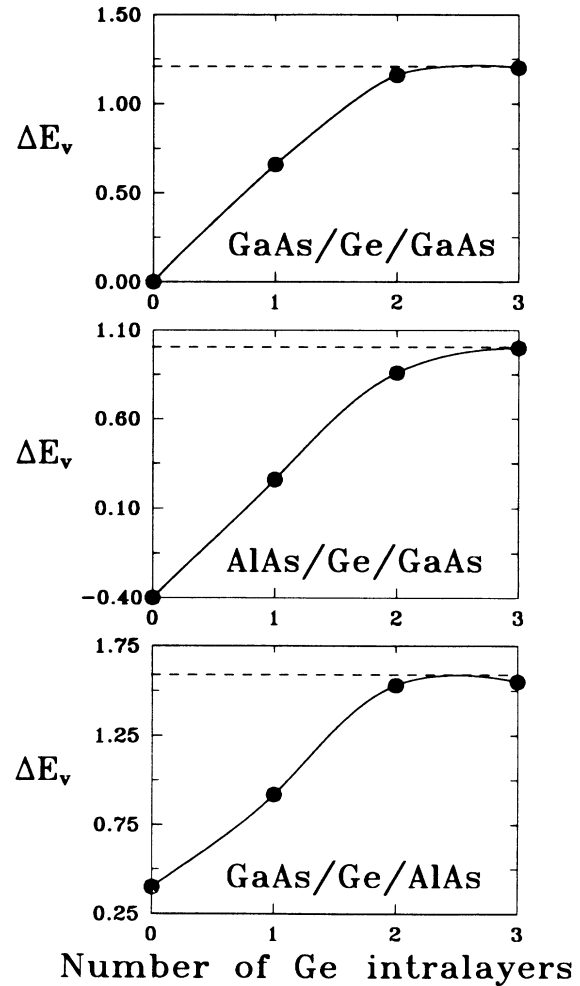


FIG. 8. Band-offset dependence on the number of Ge monolayers for (a) the homojunction GaAs/Ge/GaAs (100) and the heterojunctions (b) AlAs/Ge/GaAs and (c) GaAs/Ge/AlAs (100). The straight line corresponds to the thick intralayer limit.

$$\begin{aligned}\Delta E_v(\text{GaAs-GaAs}) &= 1.20 \text{ eV} , \\ \Delta E_v(\text{GaAs-AlAs}) &= 0.97 \text{ eV} , \\ \Delta E_v(\text{AlAs-GaAs}) &= 1.54 \text{ eV} , \\ \Delta E_v(\text{AlAs-AlAs}) &= 1.31 \text{ eV} .\end{aligned}$$

We should comment that these discontinuities are, to a large extent, the result of the electrostatic dipoles induced at the different interfaces. Thus, consider the GaAs and AlAs homojunctions: in these cases, we find the band offsets determined by the electrostatic dipoles induced at the polar-Ge interfaces (for GaAs, these two dipoles amount to 0.65 eV, while for AlAs these dipoles yield 0.77 eV), and by the electrostatic dipole induced along the Ge intralayer that equalizes the Fermi levels of both interfaces (0.55 eV for GaAs and 0.54 eV for AlAs).

Let us turn our attention to the thin intralayer limit. We have analyzed this limit by considering the cases of having one, two, or three Ge monolayers between different semiconductors. We only mention here how the band offset ΔE_v evolves in our calculation as a function of the number of Ge monolayers. Figure 8 shows our results for the homojunction GaAs/Ge/GaAs (100) and the heterojunctions AlAs/Ge/GaAs (100) and GaAs/Ge/AlAs (100).

Notice that the introduction of Ge intralayers between two semiconductors can be viewed, according to Harrison's model,¹⁹ from a transfer of protons from an As layer to an adjacent cation layer, producing a dipole in the interfacial region whose magnitude is later reduced by screening. The signs in the dipoles obtained from our calculations are in accordance with this simple view: in all junctions and for all coverages, a dipole is created which points in the sense As-X (X being the cation layer adjacent to the interface) thus tending to increase the energy in the sense As-Ge_n-X. We find this dipole strong enough to reverse the sense of the valence-band offset at AlAs/Ge/GaAs.

The main conclusion we can draw from these figures is that ΔE_v grows almost linearly with the number of monolayers between zero and two, saturating quickly when moving from two to three monolayers. Thus, for three monolayers we already reach the thick intralayer limit analyzed previously. It might seem surprising, by looking at Figs. 3(a) and 5(a), where we see that the

interface perturbation for the cation-terminated case extends up to six or seven layers inside Ge, that the thick layer limit is recovered with only three Ge monolayers; we should say, however, that most of the interface electrostatic dipole is already created between the polar semiconductors and the Ge third layer. In spite of this, it is important to stress that the electron charge at the anion-terminated interface and the hole charge at the cation-terminated interface are not spatially separated for three Ge monolayers. The results of Sec. III, the thick intralayer limit, suggest that five or six Ge monolayers are necessary for having the electron and holes spatially separated at the anion and cation interfaces, respectively.

IV. CONCLUSIONS

In this paper we have analyzed how a Ge intralayer modifies the band offsets of different homopolar and heteropolar semiconductor interfaces using a consistent tight-binding approach. Our results for one or two Ge monolayers are in good agreement with the independent results of Peressi *et al.*,¹³ calculated using a LDA approach and linear-response theory, showing a linear dependence of the band-offset modification with the number of deposited intralayers. This is very satisfactory, yielding a strong support for the method used in this paper.

The results reported here are related to the limit of a thick Ge intralayer. We have analyzed in detail this limit by considering the two ionic interfaces between Ge and the corresponding semiconductors. From the results of each interface, we have deduced the heterojunction band offset and have shown that its thick limit is recovered for three Ge monolayers. Our analysis also shows that the final band offset is basically related to the different band bendings created at the two interfaces: these band bendings are due to the different electron charges accumulated in the anionlike and cationlike interfaces.

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