Band-offset transitivity in strained (001) heterointerfaces

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Energy-band lineups at several [100] heterojunctions of III-V semiconductors are calculated using a self-consistent tight-binding treatment. The calculations exhibit transitivity to within 0.2 eV for $In_{1-x}Ga_xAs/In_{1-y}Al_yAs/InP$, GaAs/InAs/InP, GaAs/GaP/InP, and GaSb/GaAs/InAs. For $In_{1-x}Ga_xAs/In_{1-y}Al_yAs/InP$, the results are in good agreement with experimental data. For heterojunctions where the constituents share neither a common anion nor cation, the two possible interfaces do not necessarily lead to a single-band offset. This, and also the strain configuration, has to be considered when applying the transitivity rule (that is, the fact that for three semiconductors, *A*, *B*, and *C*, the band offset at the heterojunction *A*/*B* can be deduced from the band offsets at the heterojunctions *A*/*C* and *C*/*B*), provided we take care that the material *C* corresponds to the material at the interface.

Determination of band alignments at semiconductor heterojunctions from both an experimental and theoretical point of view is still the subject of many investigations. The debate for deciding whether band offsets are determined by bulk properties of the constituent materials or by interface specific dipoles is not closed.[1] The former hypothesis[2–4] obviously implies band-offset transitivity (that is, the idea that for three semiconductors *A*, *B*, and *C*, the band offset at the heterojunction *A*/*B* can be deduced from the band offset at the heterojunction *A*/*C* plus the band offset at the heterojunction *C*/*B*), whereas under the latter hypothesis, band-offset transitivity is not necessarily verified. Recently, a first-principles calculation of band offsets in the lattice-matched $In_{1-x}Ga_xAs/In_{1-y}Al_yAs/InP(001)$ systems exhibit transitivity to within 0.01 eV.[5] In this paper, we consider the same system (but lattice-matched and lattice-mismatched cases) and also several other lattice mismatched systems [GaAs/InAs/InP(001), GaAs/GaP/InP(001), GaSb/GaAs/InAs(001) and GaSb/InSb/InAs(001)]. For this, we calculate band lineups using a self-consistent tight-binding treatment, taking into account the charge transfers across the interfaces. From this study, it appears that band-offset transitivity is verified for all these heterojunctions of III-V semiconductors, even in lattice-mismatched systems, so long as it is applied to heterojunctions strained to the same substrate. We also demonstrate that when the constituents share neither common anion nor cation, the two possible interfaces do not necessarily lead to the same band offset.

If we consider *M*As/InP ($M = Ga_{1-x}In_x$ or $Al_{1-y}In_y$), two possible interfaces occur: As-In or *M*-P. As InAs and MP lattice parameters are different from InP lattice parameter, even when *M*As is lattice matched to InP, interface bonds are strained. Reference 6 describes this phenomenon fairly well and shows that, for ideal abrupt interfaces, the strain is confined to the interface layers and total-energy minimization yields a value quite close to the one based on bulk lattice constants and elastic coefficients. That is why, in order to calculate strain redistribution near the interfaces of a strained system we have extended to strained systems the work of Taguchi and Ohno[7] within Keating's formalism.[8]

Mixed alloys are described within the VCA (virtual crystal approximation). The accuracy of the VCA when alloy constituents are lattice mismatched has been checked by considering the alloy Hamiltonian as the sum of the Hamiltonians of the two strained constituents; the so calculated valence-band offsets are equivalent to the VCA calculated ones (difference less than 30 meV). The conduction-band offset is then obtained from the valence-band one by using an experimental law for the gap energy in order to take into account the bowing effect.

The semiconductors are described within the tight-binding approximation, using an sp^3s^* basis as proposed by Vogl,[9] and including the spin orbit (which is important for the band alignment when spin-orbit splittings appreciably differ from the well to the barrier). The effect of the atomic rearrangement due to strain is taken into account by the use of a power law for the dependence of the tight-binding interactions upon distance.[10] Our description provides accurate charge transfers and screening in each material.[11]

We have already set up a self-consistent tight-binding description of common atom heterojunctions which determines the charge transfers at the interface quite correctly.[12] If one wants to extend this work to systems

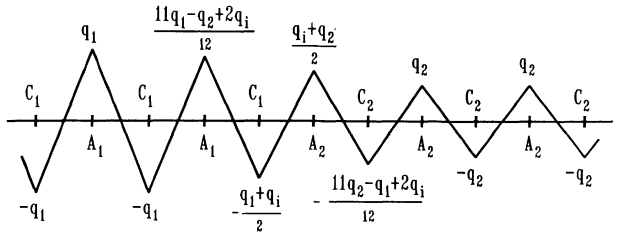

FIG. 1. Charge redistribution around the interface for the zero-dipole condition for a system where the constituents share neither common anion nor cation. q_1, q_2, and q_i are, respectively, the bulk charges of the barrier, the well, and of the interface.

TABLE I. Calculated top of valence-band offsets of the lattice-matched $Ga_{0.47}In_{0.53}As/InP$, $Al_{0.48}In_{0.52}As/InP$, and $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$ systems compared to the experimental range of results. Both zero-dipole (ZD) and self-consistent (SC) calculations are indicated.

	ZD calc. (eV)	SC calc. (eV)	Expt. meas. (eV)
$Ga_{0.47}In_{0.53}As/InP$			0.35–0.40
int. InAs	0.400	0.395	
int. $Ga_{0.47}In_{0.53}P$	0.453	0.460	
$Al_{0.48}In_{0.52}As/InP$			0.16,0.29
int. InAs	0.147	0.141	
int. $Al_{0.48}In_{0.52}P$	0.194	0.189	
$Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$	0.230	0.241	0.15–0.24

where the constituents share neither common anion or common cation, it appears that the choice of interactions crossing the interface is crucial. Here we choose to assume that an interaction crossing the interface is equivalent to the interaction in a bulk material made by the two atoms located on both sides of the interface (including strain effect, that is taking into account the fact that the atomic distribution at the interface corresponds to a strained interface material).

The self-consistent band offset obtained as just described this way can be approximated by the zero-dipole approximation. This corresponds to a charge distribution which does not induce any macroscopic dipole across the interface. Due to the important screening in semiconductors, the most physical situation is the most localized redistribution of charge. This has to be corrected in order to introduce the dielectric constant according to Ref. 13.

The charge distribution corresponding to a zero-dipole condition on four planes around the interface is indicated in Fig. 1 for a system without common atom: this condition takes into account the nature of the interface (by the use of q_i). It appears more realistic than the most localized condition which would impose the bulk charge of the interface q_i to be the average of the well and barrier bulk charges q_1 and q_2. The absolute error on resulting band offsets bound to the empirical tight-binding description of each material is estimated to about 0.1 eV. As parameters used to describe all the materials are fitted in the same way, the error on the differences between our calculated offsets for different systems should be much lower than 0.1 eV.

First we consider the system InAs/InP with interdiffusion at the interface; this is equivalent to the system InAs-$InAs_xP_{(1-x)}$-InP. In this system, the valence-band offset is quite identical to the one of the InAs/InP system (0.57 eV). This is easy to understand as the two limiting cases $x=1$ and 0 lead to the InAs/InP system. To first order, interdiffusion in systems with a common atom does not change the valence-band offset.

Let us now pass through strained systems. For the $Ga_{0.47}In_{0.53}As/InP$ lattice-matched system, the offsets for the two interfaces differ from about 50 meV. The calculated valence-band offsets in this lattice-matched case vary from 0.40 eV for the InAs interface to 0.45 eV for the $Ga_{1-x}In_xP$ interface, in the range of experimental values.[14–19] Similarly, the valence-band offset of the

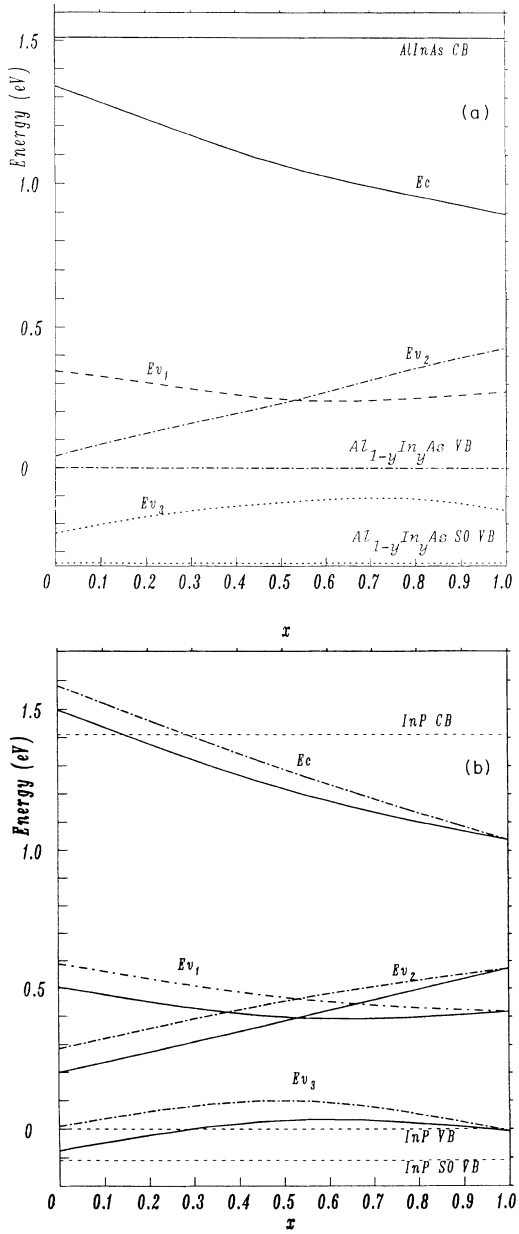

FIG. 2. Band alignments of (a) $Ga_{1-x}In_xAs/Al_{0.48}In_{0.52}As$ and (b) $Ga_{1-x}In_xAs/InP$ systems; for this latter system, dotted-dashed curves correspond to $Ga_{1-x}In_xP$ interface, solid curves to an InAs interface, and dashed curves indicate the InP band edges.

TABLE II. For the lattice-mismatched GaAs/InP [(a)] and GaSb/InP [(b)] systems, and for each interface, transitivity rule obtained and directly calculated top of valence-band offsets are compared.

	Corrected zero-dipole calculation (eV)	Self-consistent calculation (eV)
	(a)	
$(GaAs/InAs)_{InP}$	−0.082	−0.091
$(InAs/InP)_{InP}$	0.565	0.571
GaAs/InP by trans.	0.483	0.480
GaAs/InP int. InAs	0.483	0.501
$(GaAs/GaP)_{InP}$	0.210	0.207
$(GaP/InP)_{InP}$	0.397	0.362
GaAs/InP by trans.	0.607	0.569
GaAs/InP int. GaP	0.604	0.585
	(b)	
$(GaSb/InSb)_{InAs}$	−0.142	−0.138
$(InSb/InAs)_{InAs}$	0.712	0.725
GaSb/InAs by trans.	0.570	0.587
GaSb/InAs int. InSb	0.565	0.591
$(GaSb/GaAs)_{InAs}$	0.413	0.406
$(GaAs/InAs)_{InAs}$	0.175	0.166
GaSb/InAs by trans.	0.588	0.572
GaSb/InAs int. GaAs	0.576	0.560

lattice-matched $Al_{0.48}In_{0.52}As/InP$ system varies from 0.15 eV for the InAs interface to 0.19 eV for the $Al_{1-x}In_xAs$ one. This cannot explain the discrepancy between the two available experimental values reported in Table I.[20,21] However, our results are in good agreement with one of these experimental measurements. Provided one adds offsets calculated with a barrier ending with the same atom, transitivity leads to an offset value of 0.25 eV for the lattice-matched $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$ system. This is quite close to the directly calculated valence-band offset 0.24 eV and to the experimental results.[20,22–27]

Figure 2 shows for a varying In concentration the band alignments of the $Ga_{(1-x)}In_xAs/Al_{0.48}In_{0.52}As$ [Fig. 2(a)] and $Ga_{(1-x)}In_xAs/InP$ [Fig. 2(b)] systems; in this latter system, dotted curves correspond to a $Ga_{(1-x)}In_xP$ interface and the others to an InAs one. First, one can note the perfect transitivity of the system: for the InAs interface, one deduces Fig. 2(b) from Fig. 2(a) by the same constant shift, about 0.1 eV, whatever the In concentration is. This shift is the offset of the lattice-matched system $Al_{0.48}In_{0.52}As/InP$ with an InAs interface.

In the GaAs/InP system, the difference between the two possible interfaces increases to 80 meV (Table II) whereas the valence-band offsets of the GaSb/InAs system are here closer for the two types of interface: they only differ by 30 meV for the self-consistent results (Table II).

Once again transitivity leads to the same conclusion. In strained systems, we have to calculate the valence-band offset of well-interface and interface-barrier systems, both strained to the barrier. This has been done for GaAs/InP and GaSb/InAs strained systems. Observation of Table II shows that the transitivity rule is coherent within 0.02 eV with our direct calculation for GaAs/InAs/InP(001), GaAs/GaP/InP(001), GaSb/GaAs/InAs(001), and GaSb/InSb/InAs(001) once again only if we take care of the atom ending the barrier and if all materials in the system are strained to the same bulk.

In summary we have extended a band-alignment calculation method from III-V systems to III-V systems without common atoms. The interdiffusion in systems where the constituents share either common anion or cation such as InAs/InP has then been proved not to modify the offset. In the case of ideal interfaces, the transitivity rule appears to be verified within 0.02 eV for the $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$, $Ga_{0.47}In_{0.53}As/InP$, and $Al_{0.48}In_{0.52}As/InP$ lattice-matched systems as well as for the strained GaAs/InP and GaSb/InAs systems. However, depending of what atoms are at the interface, the variation of our calculated valence-band offset can change from 80 meV for the GaAs/InP system and 50 meV for the $Ga_{0.47}In_{0.53}As/InP$ and $Al_{0.48}In_{0.52}As/InP$ lattice-matched systems. The variation of the valence-band offset with the interface could, in principle, explain some dispersion of the measured band offsets. This dispersion could be related to some deviations from ideal abrupt interfaces (such as alloy segregation near the heterojunction). This is on current investigation and should be the subject of a planned forthcoming publication.

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