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## First-principles calculations of GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) band offsets

X H Zhang<sup>†</sup>, S J Chua<sup>†‡</sup>, S J Xu<sup>‡</sup> and W J Fan<sup>†</sup>

<sup>†</sup> Centre for Optoelectronics, Department of Electrical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

<sup>‡</sup> Institute of Materials Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

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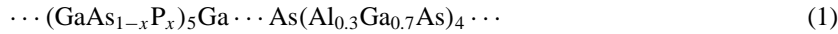
**Abstract.** The GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) band offsets are calculated for both the Ga-As and (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>) interface bonds within first-principles local density functional theory. It is found that the band offsets are independent of the type of interfacial bond, while the valence band offset, VBO, decreases linearly with  $x$  as  $VBO = 0.143 - 0.153x$  eV and the inferred conduction band offset CBO (the band-gap difference minus the valence band offset) decreases linearly as  $CBO = 0.236 - 0.590x$  eV for  $0.0 \leq x \leq 0.20$ .

The GaAsP-GaAlAs strained-layer quantum well grown on a GaAs substrate is of technological significance, mainly because of its large optical nonlinearity. Zhang *et al* [1] have demonstrated that the excitonic transition peaks can achieve an energy blue-shift as large as 33 meV during photoluminescence measurements. Thus the GaAsP-GaAlAs strained-layer quantum well is a good candidate for making optoelectronic devices such as optical switches and modulators. An accurate determination of the band offset at the GaAsP-GaAlAs strained-layer quantum well interfaces is very important for understanding its optical and transport properties. However, such a determination is complicated by the fact that, even for ideally abrupt interfaces, there are two possible different terminations: Ga-As and (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>) interface bonds. To our knowledge, neither experimental data nor calculated values of the band offset for this system have been obtained so far. In this work, we present first-principles pseudopotential virtual-crystal calculations of the GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) band offsets, for both the Ga-As and (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>) interface bonds for  $x = 0.04, 0.08, 0.12, 0.16, 0.20$ . We find that the Ga-As and (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>) interfaces have the same band offset, with both the valence band offset and conduction band offset decreasing linearly with the phosphorus composition  $x$  over the range  $0.0 \leq x \leq 0.20$ .

The valence band offset (VBO) can be written as the sum of two terms [2–6]: the band-structure contribution  $\Delta E_v$ , which is the difference between the energies of the valence band edges of the two bulk materials referred to the average electrostatic potential in the corresponding bulk material; and the electrostatic potential line-up  $\Delta V$ , due to the charge-density distribution at the interface. Each term is calculated within the framework of the density functional theory [7, 8] with the local density approximation (DFT-LDA), applied in the momentum-space formalism [9], using nonlocal norm-conserving pseudopotentials [10], and a plane-wave basis set. For the exchange–correlation potential we use the Ceperley–Alder [11] form of the LDA as parametrized by Perdew and Zunger [12]. The Brillouin zone

(BZ) integrations are performed by sampling on a regular Monkhorst–Pack (MP) mesh [13] in reciprocal space, which is equivalent to using Chadi–Cohen special points [14]. Dandrea *et al* [15, 16] have summarized the manner in which band offsets are extracted from first-principles pseudopotential-based local density functional calculations (including spin–orbit effects), and the manner in which noncommon-atom heterojunctions allow for a possible dependence of the band offset on the interfacial atomic structure. We follow their scheme in our calculations. In addition, the virtual-crystal approximation (VCA) is used to describe the alloys of GaAsP and AlGaAs. It has been shown that the first-principles virtual-crystal calculations can yield a good description of the band offset in alloys [17, 18].

In order to calculate the GaAs<sub>1-x</sub>P<sub>x</sub>–Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) valence band offsets, we perform calculations on (GaAs<sub>1-x</sub>P<sub>x</sub>)<sub>5</sub>(Al<sub>0.3</sub>Ga<sub>0.7</sub>As)<sub>4</sub> superlattices. Two such superlattices are studied: one with Ga–As interface bonds and the other with (Al<sub>0.3</sub>Ga<sub>0.7</sub>)–(As<sub>1-x</sub>P<sub>x</sub>) interface bonds. The atomic structure of the Ga–As-type superlattice is given by



while that of the (Al<sub>0.3</sub>Ga<sub>0.7</sub>)–(As<sub>1-x</sub>P<sub>x</sub>) type of superlattice is given by



Since the band offsets appropriate for strained GaAs<sub>1-x</sub>P<sub>x</sub> on unstrained Al<sub>0.3</sub>Ga<sub>0.7</sub>As (grown on a GaAs substrate) are of interest, the superlattice in-plane lattice constant  $a_{xy}$  is set equal to that of GaAs, i.e.  $a_{xy} = a_{\text{GaAs}}$  (ignoring the difference between the lattice constant of GaAs and that of AlAs). As GaAs<sub>1-x</sub>P<sub>x</sub> has a lattice constant smaller than that of Al<sub>0.3</sub>Ga<sub>0.7</sub>As, it will undergo a tetragonal distortion, as will the Ga–As and (Al<sub>0.3</sub>Ga<sub>0.7</sub>)–(As<sub>1-x</sub>P<sub>x</sub>) interface bonds.

The derivation of the electrostatic potential line-up,  $\Delta V$ , at the interface requires that one first determine the positions of the atoms of minimum energy, i.e. the structure of the interface. This should be treated on the level of a quantum-mechanical energy minimization of the system with respect to the various parameters (strains and atomic displacements). Such a study has been performed for the prototypical case of a Si–Ge heterojunction by Van de Walle *et al* [6]. Their major conclusion is that the structure of the interface can, to a very good approximation, be determined using macroscopic elasticity theory. Furthermore, the small deviations of the minimum-energy structure from the ideal structure determined by the macroscopic elasticity theory give rise to only very small changes in the calculated band offsets. Thus, in our calculations, the positions of the atoms were determined by constructing ideal interfaces following the simple macroscopic elasticity rules. No further attempt was made to actually minimize the total energy.

**Table 1.** A summary of the GaAs<sub>1-x</sub>P<sub>x</sub>–Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) valence band offsets, conduction band offsets, and the corresponding ratios CBO/ $\Delta E_g$  for various phosphorus compositions.

P composition	VBO (eV)	CBO (eV)	CBO/ $\Delta E_g$
0.04	0.137 ± 0.020	0.213 ± 0.020	0.61
0.08	0.131 ± 0.020	0.189 ± 0.020	0.58
0.12	0.125 ± 0.020	0.166 ± 0.020	0.57
0.16	0.120 ± 0.020	0.141 ± 0.020	0.54
0.20	0.112 ± 0.020	0.119 ± 0.020	0.52

Combining the band-structure term and the potential term, the valence band offset can be obtained. Convergence tests were performed with different supercell sizes, MP

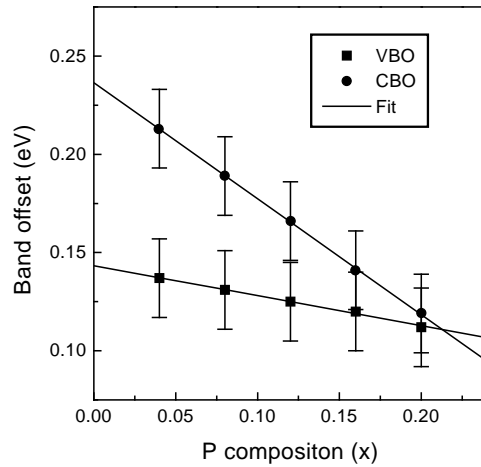
meshes, and kinetic energy cut-offs, and the relative numerical accuracy was estimated to be about 0.02 eV. The conduction band offset (CBO) can be derived from the relationship of  $\Delta E_g = \text{VBO} + \text{CBO}$ . However, the determination of the conduction band offset is not so straightforward in the present case, since the band gap is underestimated within the LDA, and the band gap of GaAs<sub>1-x</sub>P<sub>x</sub> alloy is subject to changes due to strain. Thus we use the experimental relationship [19] below to describe the energy band gap of Al<sub>y</sub>Ga<sub>1-y</sub>As:

$$E_g = 1.424 + 1.247y \quad (0.0 \leq y \leq 0.45). \quad (3)$$

On the other hand, the band gap of GaAs<sub>1-x</sub>P<sub>x</sub> without strain can be expressed as [20]

$$E_g = 1.424 + 1.150x + 0.176x^2. \quad (4)$$

However, the strain in the GaAs<sub>1-x</sub>P<sub>x</sub> layer induces shifts in the valence and conduction bands which affect the band gap. To derive the conduction band offset in the present pseudomorphic strained-layer system, a knowledge of the strain-induced changes in the band gap is necessary. We assume that the DFT-LDA is able to give the correct strain-induced band-gap changes, on the basis of the fact that the DFT-LDA works well in calculations of deformation potentials, although it underestimates the band gap. The strain-induced band-gap changes can straightforwardly be extracted from the bulk band-structure calculations. Thus, the band gap of GaAs<sub>1-x</sub>P<sub>x</sub> alloy under strain can be obtained, and the conduction band offset can be inferred from the energy band-gap difference by subtracting the valence band offset. The calculated valence band offsets, the inferred conduction band offsets, and the corresponding ratios  $\text{CBO}/\Delta E_g$  are summarized in table 1, where  $\Delta E_g$  is the band-gap difference.



**Figure 1.** The valence and conduction band offsets of GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) heterostructures with various phosphorus compositions. The linear fitted lines are also plotted.

We find that the chemically abrupt GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) interfaces have the same band offset, irrespective of the type of interfacial bond (Ga-As or (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>)). This result is in agreement with that obtained by Dandrea and co-workers for a variety of heterostructures [15]. Figure 1 shows the calculated valence band offsets and the corresponding conduction band offsets as functions of the phosphorus composition in GaAs<sub>1-x</sub>P<sub>x</sub>. For the phosphorus compositions with  $x$  such that  $0.0 \leq x \leq 0.20$ , GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) heterostructures have a type I alignment, with the top of the valence band

of GaAs<sub>1-x</sub>P<sub>x</sub> lying higher than that of Al<sub>0.3</sub>Ga<sub>0.7</sub>As, and the conduction band bottom lower than that of Al<sub>0.3</sub>Ga<sub>0.7</sub>As. Furthermore, the valence band offset, VBO, decreases linearly with  $x$  as  $VBO = 0.143 - 0.153x$  eV, while the conduction band offset decreases linearly with  $x$  as  $CBO = 0.2364 - 0.590x$  eV.

In conclusion, the first-principles pseudopotential method combined with the virtual-crystal approximation has been used to study the GaAs<sub>1-x</sub>P<sub>x</sub>-Al<sub>0.3</sub>Ga<sub>0.7</sub>As(001) band offsets. The band offset is found to be independent of the type of interfacial bond (Ga-As or (Al<sub>0.3</sub>Ga<sub>0.7</sub>)-(As<sub>1-x</sub>P<sub>x</sub>)), while both the valence band offset and the conduction band offset decrease linearly with the phosphorus composition over the range  $0.0 \leq x \leq 0.20$ .

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