Band alignment between GaAs and partially ordered GaInP

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An empirical pseudopotential method is used for calculating the band structure of partially CuPt ordered $Ga_xIn_{1-x}P$ alloy with order parameter η varying from 0 to 1. Because the relative band alignments between the binaries (GaAs, GaP, and InP) are taken into account in the pseudopotential fitting, such a calculation naturally yields the conduction and valence band alignment between the GaInP alloy and GaAs, as well as shows how the alignments change with the order parameter. The band alignment is found to change from type I to type II at $\eta=0.46$ (0.54) for $x=0.50$ (0.52), which is in good agreement with experimental data. © *2002 American Institute of Physics.*
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Because of various device applications, the band alignment for the heterostructure comprised of GaAs and $Ga_xIn_{1-x}P$ ($x\sim0.5$) has attracted a great deal of attention. Obtained by a number of different approaches,[1–23] the values for the conduction band offset $\Delta E_c=E_c(\text{GaInP})-E_c(\text{GaAs})$ range from 30 to 390 meV. It has recently been noticed that the existence of spontaneous ordering in the GaInP layer could significantly alter the band offset.[14,24–27] It thus appears that besides the possible intrinsic limitation of each technique,[1–23] the ordering effect itself might have contributed to the large scatter in the reported values, at least to some extent.

Foulon *et al.*[28] using a tight-binding method, found the valence band offset for the GaInP/GaAs heterostructure to be $\Delta E_v=320-390$ meV, depending on the microscopic structure of the interface. Froyen *et al.*[29] using a first-principle pseudopotential method, found that the band offsets between the random $Ga_{0.5}In_{0.5}P$ and GaAs are $\Delta E_c=120$ meV and $\Delta E_v=370$ meV. Their calculations further revealed that the band alignment between GaAs and a perfectly CuPt ordered GaInP, i.e., a [111] GaP/InP monolayer superlattice, would become type II with $\Delta E_c=-130$ meV and $\Delta E_v=270$ meV. However, ordering has long been known to never be perfect, which means that the ordered structure in fact should be described as a $Ga_{x+\eta/2}In_{1-x-\eta/2}P/Ga_{x-\eta/2}In_{1-x+\eta/2}P$ [111] superlattice with the so-called order parameter $\eta<1$. Thus, it is important to know the critical value η_0 at which the type I to type II transition occurs. An x-ray study of ordered GaInP has indicated that the currently achieved degree of order for this material is in the range of $\eta<0.6$.[30] If applying a widely used η^2 rule[31] to the band edge energies of Ref. 29, one will find $\eta_0=0.70$.[29] This value appears to be contradictory to the recent experimental results which have shown that ΔE_c is practically zero for ordered GaInP samples with $\eta\sim0.5$, if one compares the band gaps of the ordered samples given in Refs. 25–27 with the result of the x-ray study of Ref. 30. Therefore, a direct calculation of the band structure of a partially ordered GaInP alloy is needed for accurately determining not just the band alignment between the random GaInP and GaAs but also the type I to type II crossover point when GaInP becomes ordered.

The technique we use is an empirical pseudopotential method which was developed in Zunger's group,[32] and has recently been shown to be able to yield band gaps of partially ordered GaInP alloys in very good agreement with experimental results.[33] In the current empirical pseudopotential treatment, the band offset obtained from a large supercell containing one GaInP/GaAs interface would be the same as the band offset obtained by comparing the absolute band edges of the standalone GaInP and GaAs. Thus, we will calculate the band offsets by investigating the band edge energies of bulk GaInP and bulk GaAs separately. One might concern that this approach has ignored the possible interfacial dipole effects, so the band offset would be inaccurate. However, as indicated in Ref. 34 in general, in Ref. 11 for GaInP/GaAs, and in Ref. 35 for a similar system (InGaAs/InP), the band offset is a bulk property and insensitive to the detail interfacial dipoles as long as the interfacial atomic positions are fully relaxed. This consideration, in principle, justifies our approach to get the band offset from the individual standalone bulks. Furthermore, it is important to be pointed out that in the pseudopotential fitting procedure, the relative band offsets between the three materials GaAs, GaP, and InP have been taken into account according to the results of the first-principles full-potential linearized augmented plane wave (FLAPW)-local density approximation (LDA) calculation of Ref. 34. Here our emphasis is to investigate the effects of ordering on the bulk band structure, and in turn to obtain the band offsets between GaInP and GaAs. The accuracy of our method for determining the band offset mainly relies on the accuracy of binary band offsets. The phenomenon of partial ordering is simulated by using a large supercell with nearly 3500 atoms, according to the values of x and y. Two x values have been considered: $x=0.5$ which has been assumed in all the previous theoretical calculations and $x=0.52$ at which the $Ga_xIn_{1-x}P$ epilayer is lattice matched to the GaAs substrate at low temperature ($T\sim0$ K). The

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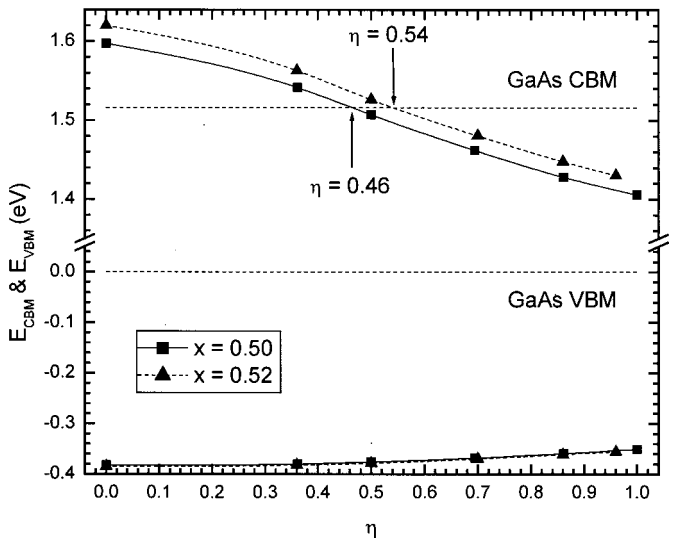

FIG. 1. Band edge energies of partially CuPt ordered $Ga_xIn_{1-x}P$ alloys, varying with order parameter η. E_{cbm}—conduction band minimum, E_{vbm}—valence band maximum.

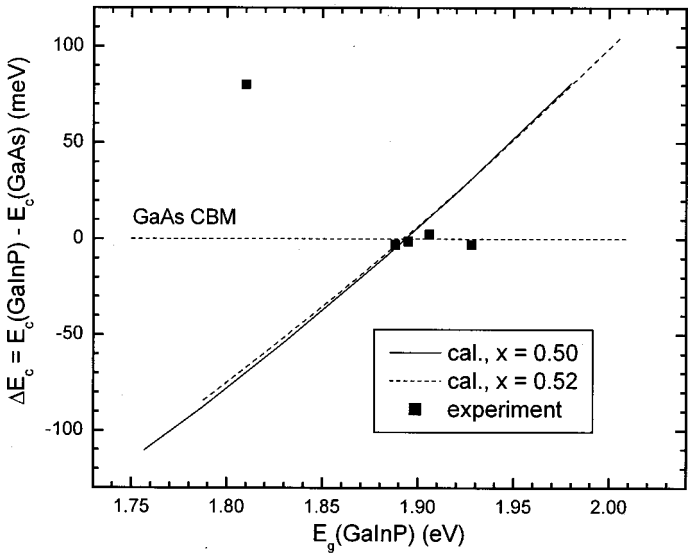

FIG. 2. Conduction band offset between partially CuPt ordered GaInP alloy and GaAs vs the band gap of the GaInP alloy. Experimental data are taken from Ref. 27.

band edge energy is obtained for each value of η by averaging over 100 or 20 configurations for $x=0.5$ and $x=0.52$, respectively. A valence force field method is used for determining the relaxed atomic configurations. Details about the implementation have been described in Ref. 33.

Figure 1 shows the variation of the band edge energies for the conduction and valence band of the CuPt ordered GaInP alloy as a function of the order parameter η. For $x=0.50$ (0.52), ΔE_c varies from +81 (104) meV at $\eta=0$ to −110 (86) meV at $\eta=1$ (0.96); ΔE varies from +383 (385) meV at $\eta=0$ to +353 (356) meV at $\eta=1$ (0.96). These results indicate that upon ordering, the change in the band gap is accommodated mostly by the downward shift of the conduction band edge, as shown in Fig. 1. Thus, the determination of ΔE_c is expected to encounter a large uncertainty if the structural parameters (e.g., the degree of ordering and composition) of the sample are not accurately known. Since the conduction band edge is much more sensitive to the composition variation, the type I to type II crossover point for the conduction band offset changes from $\eta_0=0.46$ for $x=0.50$ to $\eta_0=0.54$ for $x=0.52$. Note that the variation in η_0 between $x=0.50$ and $x=0.52$ is not due to the numerical uncertainty (which is ~1–2 meV), but the difference in the conduction band energies due to the composition difference, which is evidenced by the systematic difference (~25–20 meV), nearly independent of η, in the conduction band energies. In fact, this variation of η_0 with the conduction band energy can give a guideline for the uncertainty of so determined η_0. Note that the value of $\eta_0=0.54$ corresponds to a band gap of $E_g=1.893$ eV, which agrees quite well with most experimental data of Refs. 25–27 where $\Delta E_c\sim 0$ is found for partially ordered samples with $E_g\sim 1.9$ eV. We would like to point out that $\eta_0=0.46$ is significantly smaller than the previously predicted value of $\eta_0=0.70$,[29] since the use of the η^2 rule has now been found to be unjustified.[33] Figure 2 shows a comparison for ΔE_c vs E_g between our calculated results and the experimental data of Refs. 25–27. Note that because the ordering induced shift for the valence band is quite small, in the ΔE_c vs E_g plot of Fig. 2, the uncertainty due to not knowing the exact composition for the experimental data is expected to be negligible. A large disagreement is shown for one data point with $E_g\sim 1.82$ eV, which is likely because that particular sample had an inserted GaP layer between the GaAs and GaInP layer, the band offset had been altered, as been discussed in Refs. 27 and 36. For the other data points, the discrepancy is within the theoretical and experimental uncertainty. Also, we notice that the result of Ref. 20 (i.e., $\Delta E_c=30$ meV for an ordered GaInP sample with 60 meV band gap reduction) appears to agree quite well with the expected value, according to Fig. 2. However, we would like to point out that the finding of Ref. 6, $\Delta E_c=200$ meV not changing with ordering, is contradictory with either the experimental data of Refs. 24–27 or the theoretical results of Ref. 29 and this work.

It appears that for the random GaInP/GaAs heterojunction the conduction band offsets derived from various ''electrical measurements'' (e.g., capacitance–voltage, current–voltage),[1–12] show a larger scatter (ranging from 390 to 91 meV) as compared to those obtained from other techniques (ranging from 159 to 80 meV),[13,14,16–18] and from the previous calculation of 120 meV[29] and current calculation of 104 meV ($x=0.52$) or 81 meV ($x=0.50$). The results of the other few studies[15,19,21–23] that have yielded the valence band offset instead, ranging from 400 to 320 meV, are in general consistent with those of the above mentioned ''nonelectrical'' measurements and of the theoretical calculations. Note that for ΔE_c the results of the more recent ''electrical'' measurements (Refs. 6,10–12), except for Ref. 6, have approached those of *nonelectrical* measurements (Refs. 14–19) and the theoretical results. Figure 3 shows the comparison between our calculated results and the experimental data. For the random structure with $x=0.5$, in fact, our results agree very well with that of Ref. 29: 383 vs 370 meV for ΔE_v, 81 vs 90 meV for ΔE_c (noticing that Ref. 29 used $E_g=2.01$ eV instead of the more accurate value of 1.98 eV[33] for the random alloy). However, there is a discrepancy for the ΔE_v between this work and that of Ref. 29 for the fully ordered case: 353

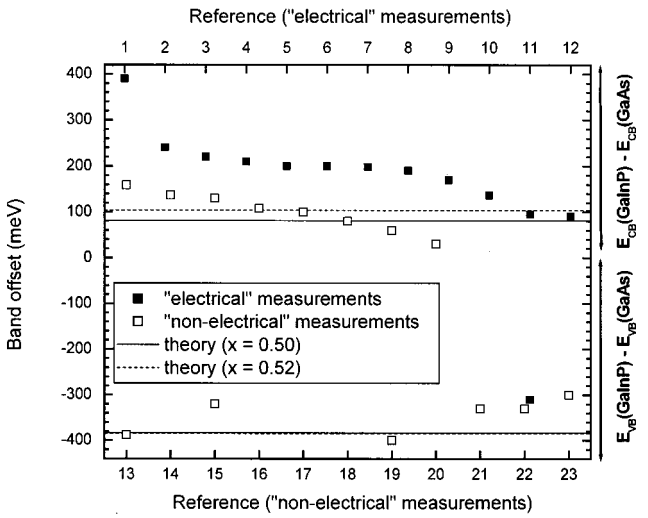

FIG. 3. Comparison between our calculated values and experimental data for the conduction and valence band offset. Tick labels indicate reference numbers.

meV of the present work versus 270 meV of Ref. 29 (the difference in ΔE_c is small: -110 meV for this work, -130 meV for Ref. 29). There could be several reasons for this discrepancy: (1) The differences of the two LDA calculations. Our band offsets are fitted to the FLAPW results of Ref. 34, while the Ref. 29 is a plane wave (PW) pseudopotential calculation. (2) The discrepancy in the value of the crystal field splitting parameter for ordered GaInP (135 meV for this calculation and 200 meV for Ref. 29). Due to this difference alone, the ΔE_v of Ref. 29 should be 30 meV smaller than our result, without affecting the conduction band. (3) The remaining difference could be due to numerical uncertainties in both Refs. 34 and 29. Despite all these uncertainties about the ΔE_v, we believe that they will not affect our conclusion about ΔE_c, since the differences for ΔE_c at $\eta=0$ or 1 between our results and those of Ref. 29 are rather small. The current study illustrates the importance of a correct η dependence for ΔE_c as well as an accurate x value for determining the crossover point η_0.

In summary, our empirical pseudopotential calculation yields for the random $Ga_xIn_{1-x}P$ ($x=0.50-0.52$)/GaAs heterostructure the conduction band offset $\Delta E_c=81-104$ meV and the valence band offset $\Delta E_v=383-385$ meV, which is in general agreement with experimental results,[10–19,21–23] and with that of previous calculations.[28,29] For the ordered $Ga_xIn_{1-x}P$ ($x=0.50-0.52$)/GaAs heterostructure, our calculation shows that the band alignment changes from type I to type II at order parameter $\eta=0.46-0.54$, and most of the band gap change is the result of ordering induced downward shift of the conduction band, which explains the experimental observations of Refs. 20 and 25–27.

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