Band offsets at GaInP/AlGaInP(001) heterostructures lattice matched to GaAs

Zhang, X. H.; Chua, S. J.; Fan, Weijun

1998

Zhang, X. H., Chua, S. J., & Fan, W. (1998). Band offsets at GaInP/AlGaInP(001) heterostructures lattice matched to GaAs. *Applied physics letters*, 73(8), 1098.

<https://hdl.handle.net/10356/80849>

© 1998 American Institute of Physics. This paper was published in *Applied Physics Letters* and is made available as an electronic reprint (preprint) with permission of American Institute of Physics. The paper can be found at the following official DOI: [<http://dx.doi.org/10.1063/1.122096>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 22:15:52 SGT

Band offsets at GaInP/AlGaInP(001) heterostructures lattice matched to GaAs

X. H. Zhang, S. J. Chua,^{a)} and W. J. Fan

Department of Electrical Engineering, Center for Optoelectronics, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

(Received 4 June 1998; accepted for publication 20 June 1998)

In this work, the band offsets at the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ heterojunction lattice matched to (001) GaAs was calculated over the whole range of aluminum composition from $x=0.0$ to 0.5 using the first-principles pseudopotential method with virtual crystal approximation. The valence band offset, VBO, varies with x as $\text{VBO}=0.433x$ eV, while the inferred conduction band offset CBO at Γ minimum (band-gap difference minus the valence band offset) varies in x as $\text{CBO}^\Gamma=0.787x$ eV. Our results are in good agreement with the experimental data. © 1998 American Institute of Physics. [S0003-6951(98)02034-8]

The (Al, Ga, In)P semiconductor alloy offers the widest direct energy gaps in the III–V semiconductors apart from nitrogen-containing compounds. This fact, combined with the possibility of lattice matching to GaAs substrate, has made GaInP/AlGaInP heterostructures lattice matched to GaAs of great interest for optoelectronic applications in the visible-wavelength region.^{1–7} Room temperature continuous wave operation of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ edge emitting¹ and vertical cavity surface emitting lasers with low threshold current density have been demonstrated.² In addition, the $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}/\text{GaAs}$ heterojunction bipolar transistors has also been successfully implemented.⁷ In all these devices, a knowledge of the band offsets is important for both their design and understanding of the operating mechanisms. Although there have been a number of reports in the literature on the conduction band offset (CBO) of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ heterostructure, most are based on low temperature photoluminescence (PL) and photoluminescence excitation (PLE) measurements and do not cover the full composition range. In this work, we calculated the band offsets at $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ (001) heterostructures lattice matched to GaAs over the whole range of aluminum composition from $x=0.0$ to 0.5 using the first-principles pseudopotential method with a virtual crystal approximation.

Both model theories^{8–12} and first-principles theories^{13–23} have been developed to determine the band offset at the heterojunction. Model theories rely on information about the bulk alone, and do not provide a complete description of the electron distribution at the interface. The only way to obtain a full picture of this effect is to perform a calculation in which the electrons are allowed to adjust to the specific environment created at the interface. This can be accomplished by performing self-consistent first-principles calculations, which will correctly describe the electrostatic potential shift that determines the band lineups. In this respect, self-

consistent first-principles calculations have shown their superiority over model theories.

In this letter, we follow the scheme as first proposed by Pickett *et al.*,²⁴ and later expanded and put on a sound footing with first-principles pseudopotentials by Van de Walle and Martin.^{13–16} Within the framework of this scheme, the valence band offset (VBO) can be written as the sum of two terms:

$$\text{VBO} = \Delta E_V + \Delta V. \quad (1)$$

Here ΔE_V , which is referred to as the band structure term, is the difference between two bulk material band edges, when the single-particle eigenvalues are measured with respect to the average of the electrostatic potential in each bulk material. This term is however characteristic of the two individual bulks, and can be evaluated from separate calculations for the two bulk materials. The second term ΔV in Eq. (1) is the difference between the macroscopic averaged electrostatic potential on the two sides of the interface, which contains all of the interface effects.

The calculations are based on density-functional theory with local density approximation (LDA),^{25,26} applied in the momentum space formalism,²⁷ using nonlocal norm-conserving pseudopotentials,²⁸ and a plane-wave basis set. For the exchange-correlation potential we use the Ceperley–Alder²⁹ form of LDA as parametrized by Perdew and Zunger.³⁰ The Brillouin zone (BZ) integrations are performed by sampling on a regular Monkhorst–Pack (MP) mesh³¹ in reciprocal space, which is equivalent to using Chadi–Cohen special points.³²

A major problem that has to be faced in calculating the electronic structure of an interface is the loss of translation symmetry, which is essential due to using a momentum space formalism of the problem. The actual interface calculations are therefore performed on a superlattice (supercell) geometry, consisting of slabs of the respective semiconductors in a particular orientation. After the self-consistent calculation on the supercell is converged, the macroscopic averaged potential $V_{\text{macro}}(z)$ of the full potential $V(x, y, z)$ throughout the supercell is obtained from relations

^{a)}Institute of Materials Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260. Electronic mail: elecsj@nus.edu.sg

$$V_{\text{macro}}(z) = \frac{2}{d} \int_{-d/4}^{+d/4} dz' \bar{V}(z+z') \quad (2)$$

and

$$\bar{V}(z) = \frac{1}{A} \int_A dx dy V(x, y, z), \quad (3)$$

where d is the lattice constant, $\bar{V}(z)$ is a planar-averaged potential, i.e., the full potential $V(x, y, z)$ averaged over a two-dimensional unit cell A in a plane parallel to the interface. Far from the interface, this planar-averaged potential $\bar{V}(z)$ is periodic over a distance $d/2$. This is a reflection of the fact that the charge density far from the interface is identical to that of the bulk material, and therefore the potential in this region must be identical to the potential of the bulk material to within a constant. The macroscopic-averaged potential as defined in Eq. (2) is thus a constant far from the interface, and the difference in the constant values on either side of the interface is simply the ΔV .

The bulk band structure calculations are performed using the zinc blende unit cell. The Brillouin zone integrations are performed by sampling on a regular $(4 \times 4 \times 4)$ MP mesh in reciprocal space, which is equivalent to using ten irreducible special $\mathbf{k}$ points. The wave functions are expanded in a plane wave basis set with a 16-Ry cutoff. For the potential lineup term, the calculations are performed based on $(\text{GaInP})_3(\text{AlGaInP})_3(001)$ superlattice geometry whose lattice constant $d = 5.6411 \text{ \AA}$ is the experimental lattice constant of GaAs substrate. The basis set consists of plane waves with a 9.0 Ry cutoff, and the $(4 \times 4 \times 4)$ MP cubic mesh appropriately folded for this geometry (equivalent to using eight irreducible special points) is used to perform the Brillouin zone integrations.

In addition, the virtual crystal approximation (VCA) is used to describe the alloys of GaInP and AlGaInP. It has been shown that the first-principles virtual crystal calculations can yield a good description of the band offset in alloys.^{33–36}

Combining the band structure term and potential lineup term, the valence band offset can be obtained. The conduction band offset can be derived from the relation $\Delta E_g = \text{VBO} + \text{CBO}$, where ΔE_g is the band-gap difference. However, the band gap is underestimated within LDA. We therefore use the experimental band gap to derive the conduction band offset. Prins *et al.*³⁷ studied the band structure of disordered $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$ system and gave the following composition dependence of the direct Γ and indirect X band gaps:

$$E_g(\Gamma) = (1.985 + 1.22x) \text{ eV} \quad (4)$$

and

$$E_g(X) = (2.282 + 0.17x) \text{ eV}. \quad (5)$$

There is a direct-indirect band-gap crossover at $x \approx 0.28$. For $x \geq 0.28$, the X conduction band minima is lower than the Γ conduction minima. We evaluated the conduction band offset for both Γ point (CBO^Γ) and X point (CBO^X), which, together with the calculated valence band offsets, are summarized in Table I and plotted in Fig. 1. For the whole composition range, $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}(001)$ hetero-

TABLE I. Summary of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}(001)$ valence band offsets (VBO), conduction band offsets (CBO), and the corresponding ratios of $\text{CBO}/\Delta E_g$ for various aluminum compositions.

Al composition	VBO (eV)	CBO^Γ (eV)	CBO^X (eV)	$\text{CBO}^\Gamma/\Delta E_g$	$\text{CBO}^X/\Delta E_g$
0.05	0.020	0.041	0.286	0.67	
0.10	0.040	0.082	0.274	0.67	
0.15	0.060	0.122	0.262	0.67	
0.20	0.083	0.161	0.248	0.66	
0.25	0.104	0.201	0.235	0.66	
0.30	0.127	0.239	0.221	0.65(0.65 ^a)	0.64
0.35	0.150	0.277	0.207	0.65(0.67 ^b)	0.58
0.40	0.174	0.314	0.191	0.64	0.52
0.45	0.198	0.351	0.176	0.64	0.47
0.50	0.222	0.388	0.160	0.64	0.42(0.33 ^c)

^aReference 38.

^bReference 39.

^cReference 41.

structures have a type I alignments with the valence band edge of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ lying higher than that of $\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}$. The valence band offset VBO is found to vary with x as $\text{VBO} = 0.433x \text{ eV}$, while the inferred conduction band offset at Γ minima CBO^Γ varies in x as $\text{CBO} = 0.787x \text{ eV}$.

Expressed as a ratio, $\text{CBO}^\Gamma/\Delta E_g$ ranges from 0.67 to 0.64 for $x = 0.05$ to $x = 0.5$. Based on PLE measurements, Liedenbaum *et al.*³⁸ obtained a ratio of $\text{CBO}^\Gamma/\Delta E_g = 0.65$ for $x = 0.3$, while Dawson and Duggan³⁹ obtained a ratio of $\text{CBO}^\Gamma/\Delta E_g = 0.67$ for $x = 0.36$. Using hydrostatic pressure PL measurement, Cockburn *et al.*⁴⁰ indicated a value of $\text{CBO}^\Gamma/\Delta E_g = 0.65$ for $x = 0.3$. Our results are in very good agreement with these experimental values. However, Yow *et al.*⁴¹ gave out the much lower $\text{CBO}/\Delta E_g$ ratios for x

FIG. 1. Composition dependence of the valence and conduction band offsets at $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}(001)$ heterostructures. (●) stands for the calculated values, the linear fitted lines (solid line) are also plotted.

>0.3 , e.g., $\text{CBO}/\Delta E_g = 0.33$ for $x=0.5$, based on internal photoemission measurements. We think, as pointed out by the authors, for $x>0.3$ their data are for X -minima transitions, and therefore the corresponding $\text{CBO}/\Delta E_g$ ratio is expressed with respect to the lower X minima rather than the Γ -minima band gap. In this case, our $\text{CBO}^X/\Delta E_g$ ratios are also rather low. For instance, our value of $\text{CBO}^X/\Delta E_g$ is 0.42 for $x=0.5$, which is in reasonable agreement with Yow *et al.*' value.

The first-principles pseudopotential method with the virtual crystal approximation is used to calculate the band offsets at $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_x\text{Ga}_{0.5-x}\text{In}_{0.5}\text{P}(001)$ heterostructures. The valence band offset VBO varies with x as $\text{VBO} = 0.433x$ eV, while the inferred conduction band offset CBO at Γ minima varies in x as $\text{CBO} = 0.787x$ eV. The values for $\text{CBO}^\Gamma/\Delta E_g$ are around 0.65. Our results are in very good agreement with the experimental data.

- ¹M. Ishikawa, Y. Ohba, H. Sugawara, M. Yamamoto, and T. Nakanisi, Appl. Phys. Lett. **48**, 207 (1986).
- ²H. Okuda, M. Ishikawa, H. Shiozawa, Y. Watanabe, K. Itaya, K. Nitta, G. I. Hatakoshi, Y. Kokubun, and Y. Uematsu, IEEE J. Quantum Electron. **QE-25**, 1477 (1989).
- ³T. Y. Wang, A. W. Kimball, G. S. Chen, D. Birkedal, and G. B. Stringfellow, J. Appl. Phys. **68**, 3356 (1990).
- ⁴S. S. Ou, J. J. Yang, R. F. Fu, and C. J. Hwang, Appl. Phys. Lett. **61**, 892 (1992).
- ⁵K. Tai, K. F. Huang, C. C. Wu, and J. D. Wynn, Electron. Lett. **29**, 1314 (1993).
- ⁶D. P. Bour, IEEE J. Quantum Electron. **30**, 594 (1994).
- ⁷H. K. Yow, P. A. Houston, C. C. Button, T. W. Lee, and J. S. Roberts, J. Appl. Phys. **76**, 8135 (1994).
- ⁸W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977).
- ⁹J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
- ¹⁰J. Tersoff, Phys. Rev. B **30**, 4874 (1984).
- ¹¹M. Cardona and L. Kleinman, Phys. Rev. B **35**, 6182 (1987).
- ¹²C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
- ¹³C. G. Van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **3**, 1256 (1985).
- ¹⁴C. G. Van de Walle and R. M. Martin, J. Vac. Sci. Technol. B **4**, 1055 (1986).
- ¹⁵C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986).
- ¹⁶C. G. Van de Walle and R. M. Martin, Phys. Rev. B **35**, 8154 (1987).
- ¹⁷D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **59**, 2091 (1987).
- ¹⁸A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).
- ¹⁹S. Baroni, R. Resta, A. Baldereschi, and M. Peressi, in *Spectroscopy of Semiconductor Microstructures*, Vol. 106 of NATO Advanced Study Institute, Series B: Physics, edited by G. Fasol, A. Fasolino, and P. Lugli (Plenum, New York, 1989), pp. 251 and 271.
- ²⁰R. Resta, L. Colombo, and S. Baroni, Phys. Rev. B **41**, 12358 (1990).
- ²¹L. Colombo, R. Resta, and S. Baroni, Phys. Rev. B **44**, 5572 (1991).
- ²²R. G. Dandrea, C. B. Duke, and A. Zunger, J. Vac. Sci. Technol. B **10**, 1744 (1992).
- ²³R. G. Dandrea and C. B. Duke, Appl. Phys. Lett. **63**, 1795 (1993).
- ²⁴W. E. Pickett, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **39**, 109 (1977).
- ²⁵P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ²⁶W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- ²⁷J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).
- ²⁸D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
- ²⁹D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- ³⁰J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ³¹H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ³²D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).
- ³³J. S. Nelson, A. F. Wright, and C. Y. Fong, Phys. Rev. B **43**, 4908 (1991).
- ³⁴S. J. Chua, X. H. Zhang, S. J. Xu, and X. Gu, J. Phys.: Condens. Matter **9**, L279 (1997).
- ³⁵X. H. Zhang, S. J. Chua, S. J. Xu, and W. J. Fan, J. Phys.: Condens. Matter **10**, 577 (1997).
- ³⁶X. H. Zhang, S. J. Chua, S. J. Xu, and W. J. Fan (unpublished).
- ³⁷A. D. Prins, J. L. Sly, A. T. Meney, D. J. Dunstan, E. P. O'Reilly, and A. R. Adams, Proceedings of the 22nd International Conference on the Physics of Semiconductors, Vancouver, Canada, August 1994.
- ³⁸C. T. H. F. Liedenbaum, A. Valster, A. L. G. J. Severens, and G. W. Hoof, Appl. Phys. Lett. **57**, 2698 (1990).
- ³⁹M. D. Dawson and G. Duggan, Phys. Rev. B **47**, 12598 (1993).
- ⁴⁰J. W. Cockburn, O. P. Kowalski, D. J. Mowbary, M. S. Skolnick, R. Teissier, and M. Hopkinson, Proceedings of the 22nd International Conference on the Physics of Semiconductors, Vancouver, Canada, August 1994.
- ⁴¹H. K. Yow, P. A. Houston, and M. Hopkinson, Appl. Phys. Lett. **66**, 2852 (1995).