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Study on valence offsets at $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunction

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Abstract. In this paper, the valence band offsets $\Delta E_v(x)$ as a function of the alloy concentration x of the heterojunctions $In_xGa_{1-x}As/In_xAl_{1-x}As$ are studied, using the average-bond-energy theory in conjunction with a cluster expansion method. It is shown that the variation in $\Delta E_v(x)$ is nearly linear and the calculation results are in very good agreement with relevant experimental data.

1. Introduction

$In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunctions are widely used in microwave and optoelectronic devices [1]. The $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterostructure devices (where the In content is about 0.3) grown on an unstrained metamorphic buffer, such as high-electron-mobility transistors, heterostructure insulated-gate field effect transistors and resonant tunnelling diodes have become of great interest recently [2]. Heterojunction devices based on the lattice-matched semiconductors $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ are of considerable interest also. Devices that use $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterointerfaces are being developed for a wide variety of optoelectronic and high-speed electronic applications.

The valence-band offsets (VBOs) (the value of ΔE_v) at semiconductor heterointerfaces are the most important parameters in determining the electrical and optical properties of heterojunctions and superlattices. Because of its importance, this topic has stimulated a great deal of experimental and theoretical research work recently. Despite the fact that several important theoretical methods for VBOs ΔE_v at lattice-matched and lattice-mismatched heterojunctions constructed by element or compound semiconductors have been presented in recent years [3], theoretical studies on $\Delta E_v(x)$ at alloy-type heterojunctions are still very scarce. In this paper, we present a theoretical method of calculating $\Delta E_v(x)$ for three-component alloy $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunctions for the first time, which consists of the average-band-energy method [4] in conjunction with the cluster expansion method, based on the LMTO-ASA band-structure method. We found that the calculation results are in very good agreement with relevant experimental data. It is shown that it is a good method to calculate the VBOs $\Delta E_v(x)$ of alloy heterojunctions using the average-band-energy method in conjunction with the cluster expansion method.

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2. Band structure and average band energy of the five ordered structures

In this paper, the band structures of the three-component alloy $In_lGa_{4-l}As_4$ and $In_lAl_{4-l}As_4$ are calculated with the LMTO ASA method. Among the five ordered structures ($l = 0, 1, 2, 3$ and 4), the $l = 0$ and 4 compounds have a zincblende (ZB) structure, the $l = 2$ compound a CuAu structure ($L1_0$), and the $l = 1$ and 3 compounds luzonite ($L1_2$) structures [5]. The lattice constants of the five ordered structures can be obtained as the average of the bulk materials GaAs, AlAs and InAs in proportion to their contents, i.e. according to the well known Vegard [6] law:

$$a_{In_lGa_{4-l}As} = (1 - l/4)a_{InAs} + (l/4)a_{GaAs} \tag{1}$$

$$a_{In_lAl_{4-l}As} = (1 - l/4)a_{InAs} + (l/4)a_{AlAs}. \tag{2}$$

After obtaining the self-consistent band structures for the five ordered structures, we determine their bonding energy E_b, antibonding energy E_a and average bond energy E_m from

$$E_b = \frac{1}{MN}\sum_{n=1}^{M}\sum_{k} E_n(\boldsymbol{k}) \tag{3}$$

$$E_a = \frac{1}{MN}\sum_{n=M+1}^{2M}\sum_{k} E_n(\boldsymbol{k}) \tag{4}$$

$$E_m = (E_b + E_a)/2 \tag{5}$$

respectively, where N is the number of unit cells and M the number of valence bands. For the ZB, $L1_0$ and $L1_2$ structures, M is set equal to 4, 8 and 16, respectively. The special-K-point method [7] is adopted for the summation over the Brillouin zone. From the test calculation of AlAs and GaAs, we find that the values of the average bond energy E_m, the valence band maximum E_v and the valence offset parameter E_{mv} given by the two-special-K-point calculation are different from those given by the ten-special-K-point calculation by about 0.1 eV, 0.2 eV and 0.07 eV respectively. However, the difference in the VBO values of AlAs/GaAs given by two methods is smaller than 0.001 eV. It is shown that there are some effects on the E_m-, E_v- and E_{mv}-values of bulk materials using the calculation of a different number of special K points, but few effects on the VBO values of the heterojunction. Therefore, in this paper, two special K points are used for the ZB and $L1_0$ structures and only one special K point $(2\pi/a)(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ [8], which corresponds to the two special K points for the ZB structure, is used for the $L1_2$ structure. In Christensen's [9] supercell calculations for VBO determination, he treated the cation's shallow d orbitals as core and valence states, respectively, and took the average of the two VBO values as the final result so as to include the effects of the cation's shallow orbitals on the VBO value. In the same consideration, we take the Ga 3d and In 4d orbitals as core states (i.e. only s, p states are taken as valence states) and valence states (i.e. s, p, d states are all taken as valence states), respectively, for the band-structure calculations of the five ordered structures in this paper. The two treatments are noted as approach 1 (as core states) and approach 2 (as valence states), respectively, hereafter. The results of bonding energy E_b, antibonding energy E_a, average bond energy E_m and the valence band maximum E_v for the five ordered structures of $In_lGa_{4-l}As_4$ and $In_lAl_{4-l}As_4$ given by the two approaches are listed in table 1.

Table 1. Results of bonding energy E_b, antibonding energy E_a, average bond energy E_m and the valence-band maximum E_v as well as the valence offset parameter E_{mv} for the five ordered structures of $In_lGa_{4-l}As_4$ and $In_lAl_{4-l}As_4$, given by approaches 1 and 2 as stated in the text.

	Approach 1					Approach 2				
	E_{b1} (eV)	E_{a1} (eV)	E_{m1} (eV)	E_{v1} (eV)	E_{mv1} (eV)	E_{b2} (eV)	E_{a2} (eV)	E_{m2} (eV)	E_{v2} (eV)	E_{mv2} (eV)
$l=0$ GaAs	−6.605	3.651	−1.477	−1.363	−0.114	−6.614	3.832	−1.391	−1.133	−0.258
$l=1$ $In_1Ga_3As_4$	−6.585	3.477	−1.554	−1.451	−0.103	−6.594	3.626	−1.484	−1.237	−0.247
$l=2$ $InGaAs_2$	−6.577	3.301	−1.638	−1.555	−0.083	−6.590	3.419	−1.586	−1.360	−0.226
$l=3$ $In_3Ga_1As_4$	−6.577	3.123	−1.727	−1.682	−0.045	−6.597	3.211	−1.693	−1.502	−0.191
$l=4$ InAs	−6.585	2.944	−1.820	−1.814	−0.006	−6.614	3.004	−1.805	−1.650	−0.155
$l=0$ AlAs	−6.251	3.680	−1.285	−1.629	0.344					
$l=1$ $In_1Al_3As_4$	−6.322	3.508	−1.407	−1.636	0.229	−6.328	3.519	−1.405	−1.615	0.210
$l=2$ $InAlAs_2$	−6.402	3.330	−1.536	−1.652	0.116	−6.417	3.354	−1.531	−1.586	0.055
$l=3$ $In_3Al_1As_4$	−6.490	3.141	−1.675	−1.733	0.058	−6.513	3.182	−1.666	−1.628	−0.038
$l=4$ InAs	−6.585	2.944	−1.820	−1.814	−0.006	−6.614	3.004	−1.805	−1.650	−0.155

3. The valence-band offsets parameter of the alloys

The value of the band offsets of heterojunction is mainly determined by the band offset parameter (E_{mv}, i.e. $E_m - E_v$) of the five ordered semiconductor structures. We can write the band offset parameters E_{mv} of $In_lGa_{4-l}As_4$ and $In_lAl_{4-l}As_4$ given by two approaches as follows:

$$E_{mv1} = E_{m1} - E_{v1} \tag{6}$$

$$E_{mv2} = E_{m2} - E_{v2}. \tag{7}$$

The band offset parameter of the alloys $In_xGa_{1-x}As$ and $In_xAl_{1-x}As$ can be obtained by making use of the cluster expansion method, in terms of the data of the five ordered structures listed in table 1, i.e.

$$E_{mv1}(x) = \sum_l P_l(x) E^l_{mv1} \tag{8}$$

$$E_{mv2}(x) = \sum_l P_l(x) E^l_{mv2} \tag{9}$$

where the statistical weight $P_l(x) = \begin{pmatrix} 4 \\ l \end{pmatrix} x^l(1-x)^{4-l}$ is the possibility that the l short region ordered structure occurs in the alloy. The regressed two-order polynomials for $E_{mv1}(x)$, and $E_{mv2}(x)$ are

$$In_xGa_{1-x}As: E_{mv1}(x) = 0.063x^2 + 0.046x - 0.114 \tag{10}$$

$$E_{mv2}(x) = 0.053x^2 + 0.052x - 0.259 \tag{11}$$

$$In_xAl_{1-x}As: E_{mv1}(x) = 0.132x^2 - 0.481x + 0.344 \tag{12}$$

$$E_{mv2}(x) = 0.080x^2 - 0.578x + 0.345. \tag{13}$$

The $E_{mv1}(x)$ and $E_{mv2}(x)$ curves of $In_xGa_{1-x}As$ are shown in figure 1, and those of $In_xAl_{1-x}As$ are shown in figure 2. Comparing $E_{mv1}(x)$ and $E_{mv2}(x)$ curves in figure 1 and figure 2, we can find that the results given by approach 1 are somewhat higher than those from approach 2. The curve of $E_{mv1}(x)$ is nearly parallel to $E_{mv2}(x)$ with the Ga

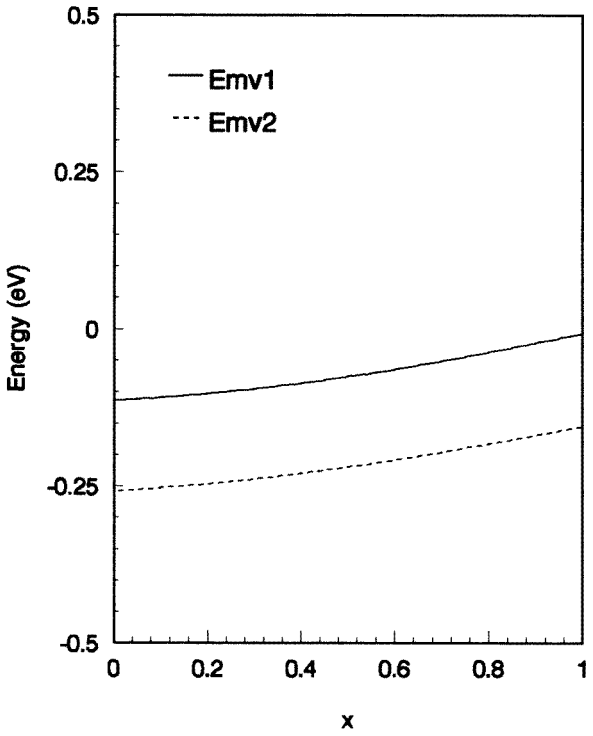

Figure 1. $E_{mv}(x)$ of $In_xGa_{1-x}As$ as a function of x. The $E_{mv1}(x)$ curves are given by approach 1; the $E_{mv2}(x)$ curves are given by approach 2.

concentration increasing in $In_xGa_{1-x}As$, but the differences between $E_{mv1}(x)$ and $E_{mv2}(x)$ increase with increasing Al concentration in $In_xAl_{1-x}As$.

4. Determination of the valence band offset at the $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunctions

For the determination of the VBO at an A/B heterojunction, the average-bond-energy theory requires only the calculations for bulk materials A and B to determine their average bond energy E_m and the valence band maximum E_v. Then the $\Delta E_v(x)$-values can be obtained by aligning the average bond energy E_m in materials A and B:

$$\Delta E_v(x) = [E_m^B(x) - E_v^B(x)] - [E_m^A(x) - E_v^A(x)] \tag{14}$$

i.e.

$$\Delta E_v(x) = E_{mv}^B(x) - E_{mv}^A(x). \tag{15}$$

So we can write $\Delta E_{v1}(x)$ with approach 1 as the regressed two-order polynomial

$$\Delta E_{v1}(x) = 0.069x^2 - 0.527x + 0.459 \tag{16}$$

and $\Delta E_{v2}(x)$ with approach 2 can be written as

$$\Delta E_{v2}(x) = 0.027x^2 - 0.630x + 0.604. \tag{17}$$

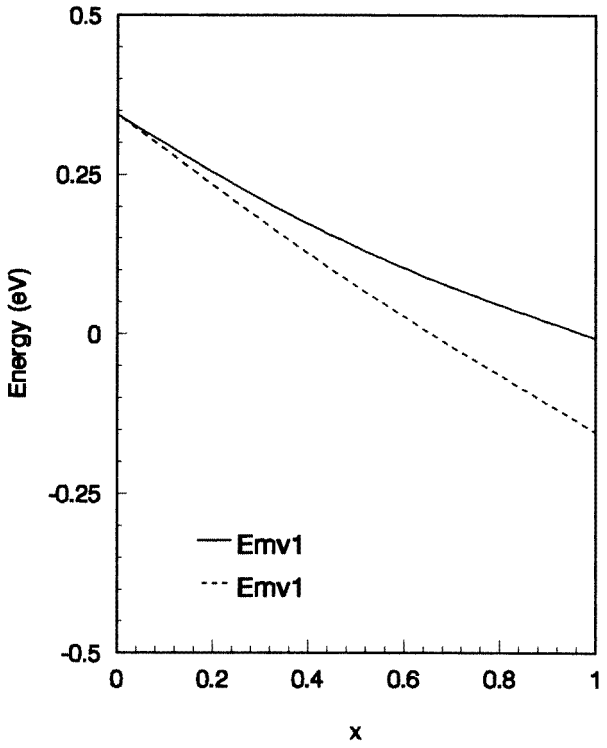

Figure 2. The $E_{mv}(x)$ of $In_xAl_{1-x}As$ as a function of x. The $E_{mv1}(x)$ curves are given by approach 1; the $E_{mv2}(x)$ curves are given by approach 2.

We can obtain the average value of $\Delta E_v(x)$ as $\Delta E_v(x) = (\Delta E_{v1}(x) + \Delta E_{v2}(x))/2$, i.e.

$$\Delta E_v(x) = 0.048x^2 - 0.578x + 0.532. \tag{18}$$

These results are shown in figure 3 by a solid line together with the results from the relevant experimental data. The detailed values of the VBO in the five ordered structures and the alloy-type heterojunctions are listed in table 2. From equation (18) and figure 3, we can see that the $\Delta E_v(x)$-value of $In_xGa_{1-x}As/In_xAl_{1-x}As$ is a function of x, and the $\Delta E_v(x)$-value decreases with increasing x, i.e. with increasing In content (i.e. decreasing Ga and Al contents). Equation (18) shows that the second-order coefficient which is characteristic of the bending of the $\Delta E_v(x)$ curve is very small (0.048), and the change in $\Delta E_v(x)$ with x is nearly linear. Therefore, the $\Delta E_v(x)$-values of the alloy $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunctions can be obtained approximately by linear regression from the ΔE_v-values of the bulk materials GaAs, AlAs and InAs.

5. Conclusions

In this paper, we present a theoretical method of calculating $\Delta E_v(x)$ for the three-component alloy $In_xGa_{1-x}As/In_xAl_{1-x}As$ heterojunctions. The average-bond-energy method [4], in which the average bond energy is used as a reference level for VBO determination, requires very little computational effort and has shown satisfactory accuracy for a series of lattice-matched and lattice-mismatched heterojunctions [3, 4].

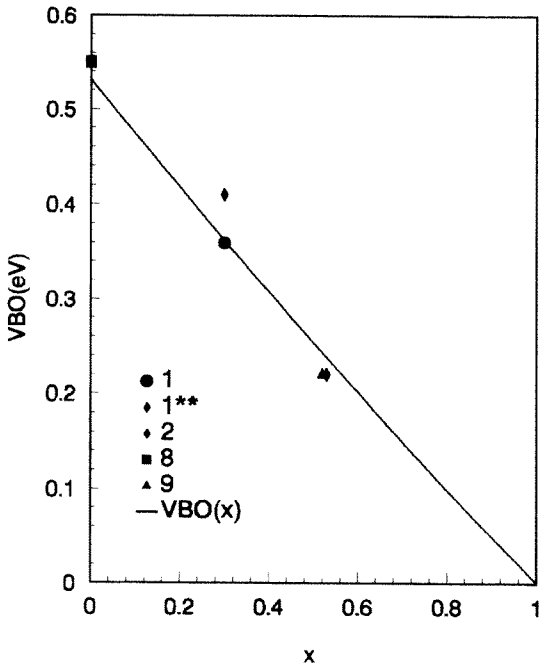

Figure 3. The variation in the VBO at $In_xGa_{1-x}As/In_xAl_{1-x}As$ with x (solid line) and relevant experimental data. (1^{**} is quoted from [1].)

Table 2. The calculated values of the VBO for the five ordered structure heterojunctions $In_lGa_{1-l}As/In_lAl_{1-l}As$ ($l = 0$, 1, 2, 3 and 4) given by the two In 4d orbital treatments and Ga 3d orbital treatments (i.e. ΔE_{v1} and ΔE_{v2}) and their average (ΔE_v), and the corresponding $\Delta E_v(x)$ for the heterojunction $In_xGa_{1-x}As/In_xAl_{1-x}As$.

	ΔE_{v1} (eV)	ΔE_{v2} (eV)	ΔE_v (eV)	$\Delta E_v(x)$ (eV)
$l = 0$ GaAs/AlAs	0.458	0.602	0.530	0.532
$l = 1$ $In_1Ga_3As_4/In_1Al_3As_4$	0.333	0.457	0.395	0.390
$l = 2$ $InGaAs_2/InAlAs_2$	0.198	0.280	0.239	0.254
$l = 3$ $In_3Ga_1As_4/In_3Al_1As_4$	0.103	0.153	0.128	0.125
$l = 4$ InAs/InAs	0.000	0.000	0.000	0.000

Comparing the $\Delta E_v(x)$-values of $In_xGa_{1-x}As/In_xAl_{1-x}As$ (listed in table 3, when $x = y$ and when x is very close but not equal to y) with the experimental data, we find that the present results are in good agreement with the experimental data for different concentrations x. It is shown that the average-band-energy method in conjunction with the cluster expansion method is an effective method for calculating the VBOs of multi-component alloy-type heterojunctions.

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Table 3. The experimental data on the VBOs (ΔE_v) of $In_xGa_{1-x}As/In_yAl_{1-y}As$ heterojunctions compared with the theoretical data in this work.

		ΔE_v (eV) for the following (x, y)				
Reference	$Q_c(=\Delta E_c/\Delta E_g)$	(0,0)	(0.3, 0.29)	(0.3, 0.3)	(0.52, 0.52)	(0.53, 0.52)
This work	0.657[a]	0.532	0.367	0.363	0.244	0.243
[1]	0.66		0.36			
[1][b]	0.62		0.41			
[2]	0.68					0.22
[10]		0.55				
[11]	0.72				0.22	
[12]	0.650					

[a] When $(x, y) = (0.3, 0.29)$, $\Delta E_g = 1.07$, $\Delta E_c = \Delta E_g - \Delta E_v = 0.703$ and $Q_c = \Delta E_c/\Delta E_g = 0.657$.
[b] Quoted from [1].

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