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Valence-band offset at $Al_xGa_{1-x}As/GaAs$: Application of average-bond-energy theory in conjunction with the cluster expansion method

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We suggest a theoretical method for the determination of valence-band offsets at alloy-type heterojunctions that is based on average-bond-energy theory in conjunction with a cluster expansion method. The application of this method to $Al_xGa_{1-x}As/GaAs$ produces results in very good agreement with relevant experimental data.

I. INTRODUCTION

Despite several important theoretical methods for valence-band offsets (VBO's) at lattice-matched heterojunctions[1–8] presented in recent years, the theoretical studies on the VBO at alloy-type heterojunctions (ATHJ's) are still very scarce. An important means is the virtual-crystal approximation (VCA). Nelson, Wright, and Fong[9] applied the VCA in their *ab initio* pseudopotential calculation to the ATHJ $Al_xGa_{1-x}As/GaAs$. In this paper, we suggest a theoretical method for the determination of the VBO at ATHJ's, which makes use of the average-bond-energy (ABE) method[8] in conjunction with the cluster expansion method.[10,11] For $Al_xGa_{1-x}As/GaAs$, this method includes three calculations: (i) band-structure and ABE calculations for five ordered structures $Al_lGa_{4-l}As_4$ ($l=0,1,2,3,4$), which correspond to the composition $x=0$, 0.25, 0.5, 0.75, and 1.0 in the ATHJ, respectively; (ii) Determination of the valence-band maximum E_v and the average bond energy E_m in Al_xGa_{1-x} by the cluster expansion method, using the data of E_v and E_m of the five ordered structures; and (iii) determination of the VBO at $Al_xGa_{1-x}As/GaAs$ by the ABE method, which uses the ABE as a reference level for VBO determination. The details of the method and results follow.

II. BAND-STRUCTURE AND ABE CALCULATIONS FOR THE FIVE ORDERED STRUCTURES

Among the five ordered structures[12] ($Al_lGa_{4-l}As_4$), $l=0$ and 4 correspond to GaAs and AlAs [zinc-blende (ZB) structure], respectively. $l=1$ and 3 (namely, $Al_1Ga_3As_4$ and $Al_3Ga_1As_4$) are a Luzonite ($L12$) structure and $l=2$ ($AlGaAs_2$) the CuAu structure (labeled by $L10$). In this paper, we make use of the linearized-muffin-tin-orbital band-structure method in the atomic sphere approximation to complete the band-structure calculations for the five ordered structures. As usual, the so-called "empty spheres" are added to the interstitial regions in the lattice structures.[13] The special-k-point method[14] is adopted for the summation over the Brillouin zone. Two special **k** points are used for ZB and $L10$ structures and only one special **k** point $(2\pi/a)(\frac{1}{4},\frac{1}{4},\frac{1}{4})$,[12] which corresponds to the two-special **k** points for the ZB structure, is used for the $L12$ structure. From the test calculation for AlAs/GaAs, we find that the VBO value given by the two-special-**k**-point calculation is different from that given by the ten-special-**k**-point calculation by only an amount smaller than 0.01 eV.

After getting the self-consistent band structures for the five ordered structures, we determine their bonding energy, antibonding energy, and average bond energy by, respectively,[15,16]

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

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

$$E_m=(E_b+E_a)/2\ , \tag{3}$$

where N is the number of unit cells and M the number of valence bands (also the number of the "important conduction bands" formed mainly by s and p states). For the ZB, $L10$, and $L12$ structures, M is evaluated by 4, 8, and 16, respectively. In Christensen's supercell calculations[2] 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's 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 $3d$ orbitals and as core states and 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. Table I lists the results given by the two approaches.

III. DETERMINATION OF THE ABE AND THE VBM FOR $Al_xGa_{1-x}As$

The determinations of the average bond energy $E_m(x)$ and the valence-band maximum $E_v(x)$ for $Al_xGa_{1-x}As$ are completed by making use of the cluster expansion method,[10,11] in terms of the data of the five ordered structures listed in Table I:

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TABLE I. Results of bonding energy E_b, antibonding energy E_a, and average bond energy E_m as well as the valence-band maximum E_v (all in eV) for the five ordered structures, given by approaches 1 and 2 as stated in the text.

		Approach 1				Approach 2			
		E_{b1}	E_{a1}	E_{m1}	E_{v1}	E_{b2}	E_{a2}	E_{m2}	E_{v2}
$l=0$	GaAs	−6.589	3.682	−1.454	−1.313	−6.599	3.863	−1.368	−1.083
$l=1$	$Al_1Ga_3As_4$	−6.497	3.696	−1.402	−1.387	−6.505	3.823	−1.341	−1.230
$l=2$	$AlGaAs_2$	−6.405	3.706	−1.350	−1.440	−6.410	3.788	−1.311	−1.311
$l=3$	$Al_3Ga_1As_4$	−6.314	3.721	−1.296	−1.510	−6.316	3.759	−1.279	−1.465
$l=4$	AlAs	−6.223	3.740	−1.242	−1.561				

$$E_m(x)=\sum_l P_l(x)E_m^l \ , \tag{4}$$

$$E_v(x)=\sum_l P_l(x)E_v^l \ , \tag{5}$$

where the statistic weight $P_l=\binom{4}{l}x^l(1-x)^{4-l}$ is the possibility of the l short region ordered structure taking place in the alloy. Figure 1 shows the calculated results of E_m and E_v for the ATHJ and the five ordered structures, by the two approaches to Ga 3*d* orbitals (labeled by subscripts 1 and 2, respectively). The regressed two-order polynomials for $E_{m1}(x)$ and $E_{v1}(x)$ are

$$E_{m1}=-1.454+0.207x+0.005x^2 \ , \tag{6}$$

$$E_{v1}=-1.313+0.281x+0.033x^2 \ . \tag{7}$$

Those for E_{m2} and E_{v2} are

$$E_{m2}=-1.368+0.107x+0.019x^2 \ , \tag{8}$$

$$E_{v2}=-1.083+0.541x+0.063x^2 \ . \tag{9}$$

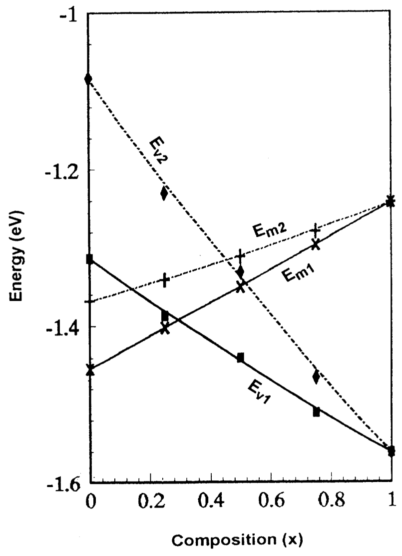

FIG. 1. The calculated E_m and E_v results. The E_{m1} and E_{v1} curves are given by approach 1 and the E_{m2} and E_{v2} by approach 2. The *x*, ■, +, and ◆ denote the calculated values of E_{m1}, E_{v1}, E_{m2}, and E_{v2}, respectively, for the five ordered structures.

Comparing E_{m1} and E_{v1} curves with E_{m2} and E_{v2} in Fig. 1, we find that the results given by approach 2 are somewhat higher than those from approach 1. Their differences increase with the composition of Ga in increasing $Al_xGa_{1-x}As$.

IV. DETERMINATION OF THE VBO AT THE HETEROJUNCTION $Al_xGa_{1-x}As/GaAs$

For the determination of the VBO at a heterojunction *A*/*B*, the ABE method requires only the calculations for bulk materials *A* and *B* for determining their average bond energy E_m and the valence-band maximum E_v. Then the VBO value can be obtained by aligning the two ABE's values in materials *A* and *B*,

$$\Delta E_v(x)=[E_m^A(x)-E_v^A(x)]-[E_m^B(x)-E_v^B(x)] \ . \tag{10}$$

We note the two results from the two approaches to Ga 3*d* orbitals by subscripts 1 and 2 (namely, ΔE_{v1} and ΔE_{v2}), respectively, and take the average of $\Delta E_{v1}(x)$ and $\Delta E_{v2}(x)$, i.e., $\Delta E_v(x)=[\Delta E_{v1}(x)+\Delta E_{v2}(x)]/2$, as the final result for $Al_xGa_{1-x}As/GaAs$. These results are shown in Fig. 2 by a solid line together with the results

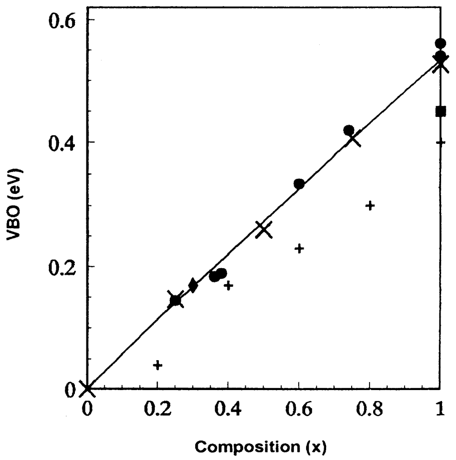

FIG. 2. The variation of the VBO at $Al_xGa_{1-x}As/GaAs$ with the composition *x* (solid line) and those results for the five ordered structure heterojunctions (×) as well as relevant experimental data: ●, Ref. 17; ◆, Ref. 18; ■, Ref. 19. + labels the results from the self-consistent interface calculation in Ref. 9.

TABLE II. The calculated values of the VBO for the five ordered structure heterojunctions $\mathrm{Al}_l\mathrm{Ga}_{4-l}\mathrm{As}_4$/GaAs ($l=0,1,2,3,4$) given by the two Ga 3*d* orbitals treatments (i.e., ΔE_{v1} and ΔE_{v2}) and their average (ΔE_v), and the corresponding results for the heterojunction $\mathrm{Al}_x\mathrm{Ga}_{1-x}$ As/GaAs (all in eV).

	Approach 1	Approach 2	Average ΔE_v	$\Delta E_v(x)$
GaAs/GaAs	0.000	0.000	0.000	0.000
$\mathrm{Al}_1\mathrm{Ga}_3\mathrm{As}_4$/GaAs	0.126	0.174	0.150	0.141
AlGaAs_2/GaAs	0.231	0.305	0.268	0.274
$\mathrm{Al}_3\mathrm{Ga}_1\mathrm{As}_4$/GaAs	0.355	0.471	0.413	0.406
AlAs/GaAs	0.460	0.604	0.532	0.532

from the *ab initio* pseudopotential calculation[9] and relevant experimental data.[17–19] The detailed values of the VBO in the five ordered structures and the ATHJ are listed in Table II. The curve of $\Delta E_v(x)$ in Fig. 2 can be expressed by a two-order polynomial

$$\Delta E_v(x)=0.564x-0.032x^2\ . \tag{11}$$

V. CONCLUSION

The ABE method, 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.[15,16] In regard to the Ga 3*d* orbitals effect, the present approach is similar to Christensen's[2] supercell calculations for VBO determination. From Table I and Fig. 1 we find that the effect of Ga 3*d* orbitals is to push the E_v and E_m up in energy. As a result of an increase of E_v larger than that of E_m, the VBO values given by approach 2 are relatively larger than those given by approach 1, and this increase becomes larger with the composition of Ga in the increasing ATHJ (see the "approach 1" and "approach 2" columns in Table I). For AlAs/GaAs, the average VBO value given by the ABE method is 0.532 eV, consistent with the result 0.53 from Christensen's supercell calculation using a (7+7) supercell. Our result is also in good agreement with the recent experimental data of 0.42,[20] 0.45,[19] and 0.55 eV.[17]

Comparing the VBO values of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$/GaAs (solid line in Fig. 2) with the experimental data, we find that the present results are in good agreement with the experimental data in Ref. 17 for a different composition x. Reference 17 gave a relationship between the VBO value and x as $\Delta E_v(x)=0.55x$ eV. The present result is $\Delta E_v(x)=0.564x-0.032x^2$. The coefficient of the two-order term is very small (0.032) and the slope rate of the one order term 0.564 is consistent with the experimental value 0.55. Recently, Ref. 18 obtained a VBO value of 0.17 ± 0.04 eV for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$/GaAs with $x=0.30$. The present result is 0.168 eV. The two values are consistent. In Fig. 2 it seems that our results are in better agreement with the relevant experimental data than with those from the *ab initio* pseudopotential calculation in Ref. 9.

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