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Average bonding–antibonding energy at semiconductor heterojunctions and its application to calculating the valence band offset

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Abstract. In this paper, the alignment of the average bonding–antibonding energy E_m between the two sides of heterojunctions and other relevant behaviour have been investigated. This study is based on the peculiarity of the atomic sphere approximation in the linear muffin-tin orbital band-structure calculation. Using E_m as an energy reference, we have determined the valence band offset ΔE_v -values for 16 heterojunctions. The calculated results are in excellent agreement with the available experimental data, and the computational effort required is very small.

1. Introduction

In several theoretical models of heterojunction valence band offsets ΔE_v , a reference level which is aligned on the two sides of the heterojunctions was researched in order to determine the ΔE_v -value. For example, the effective midgap energy E_B of the charge-neutrality-point (CNP) model [1, 2] and E_D of the dielectric-midgap-energy model (DME) [3] as well as the average sp^3 hybrid energy E_h of the 'pinned' model in tight-binding (TB) theory [4] are the reference levels suggested by different researchers.

Recently, we have also suggested a theoretical method [5] for ΔE_v which took the average of the bonding energy and antibonding energy (it is called the 'average bond energy' hereafter) E_m as a reference level. In this paper, we apply this method to the ΔE_v calculations for 16 lattice-matched heterojunctions. The results show excellent agreement with experimental data, and the accuracy is comparable with that of those of the more elaborate self-consistent supercell interface calculations by the norm-conserving pseudopotential method (SCIC) [6] and by the atomic sphere approximation (ASA) of the linear muffin-tin orbital (LMTO) method (SCSC) [7].

2. Method of ΔE_v calculation

In the ΔE_v calculation of the TB 'pinned' method [4], for a heterojunction A–B, the maximum energy E_v of the valence band and the average sp^3 hybrid energy E_h were

determined by TB theory. Then, the ΔE_v -value ($= [E_h(A) - E_v(A)] - [E_h(B) - E_v(B)]$) was found. Similarly, in our ΔE_v calculation of a heterojunction A-B, first the band structures and state densities of the materials A and B are determined by the scalar relativistic LMTO method. Then, the bonding energy E_b , antibonding energy E_a and average bond energy E_m are obtained from the following equations [8, 9]:

$$E_b = \frac{1}{4N} \sum_{n=1}^4 \sum_{\mathbf{k}} E_n(\mathbf{k}) = \frac{1}{4} \int E \rho_v(E) dE \quad (1)$$

$$E_a = \frac{1}{4N} \sum_{n=5}^8 \sum_{\mathbf{k}} E_n(\mathbf{k}) = \frac{1}{4} \int E \rho_c(E) dE \quad (2)$$

$$E_m = \frac{1}{2}(E_b + E_a). \quad (3)$$

Here, N is the number of unit cells, $E_n(\mathbf{k})$ is the energy eigenvalue and $\rho_v(E)$ and $\rho_c(E)$ are the total state densities of the four valence bands and the four lowest conduction bands, respectively. Finally, ΔE_v can be expressed as

$$\Delta E_v = [E_m(A) - E_v(A)] - [E_m(B) - E_v(B)]. \quad (4)$$

It is obvious that the accuracy of this ΔE_v calculation depends on the aligning situation of $E_m(A)$ and $E_m(B)$ at the heterojunction and the accuracy of the E_v - and $(E_m - E_v)$ -values given by the band-structure and bond energy calculations. In the CNP [1, 2], DME [3] and TB 'pinned' [4] methods, a reference level (E_B , E_D or E_h) which aligns at heterojunctions was assumed according to the neutral solid or dielectric screening effect without a direct numerical test. In contrast with these, in the present method, the alignment of E_m at interfaces can be numerically tested by the bond energy calculation for superlattice molecular layers (this will be discussed in the next section).

The muffin-tin basis in the LMTO ASA method [10] can be written as

$$\chi_{L'}^k(\mathbf{r}) = \frac{\Phi_{ilm}(-l-1, \mathbf{r}-\mathbf{q})}{\sqrt{s_l/2}\Phi_{il(-)}} \delta_{\mathbf{q}'\mathbf{q}} - \sum_{l'm'} \frac{\Phi_{l'm'}(l', \mathbf{r}-\mathbf{q}')}{2(2l'+1)\sqrt{s_{l'}}/2\Phi_{l'l(+)}} S_{L'L}^k. \quad (5)$$

Here, $L = q, t, l, m$ (q, t and l, m are the indices of the atomic sphere positions and the states, respectively), $S_{L'L}^k$ is the structure constant and the rest of the notation consists of the normal potential parameters [10]. In normal LMTO calculations, $l'm'$ and lm include s, p, d states. Here the d state is the higher partial wave (unoccupied) and the outermost d electrons of atoms are treated as core electrons. In this paper, we let these higher d partial waves fold down according to the Löwdin [11] perturbation scheme [12], i.e. we let the $l'm'$ in the last term in equation (5) (namely the tail of the MT basis) include s, p, d states, while the lm in the MT basis includes s, p states only. We apply this treatment to two atoms in the unit cell of Si, Ge, AlP, AlAs and AlSb (the d_{LL} approach). For the materials ZnSe, ZnTe, CdTe and HgTe, we treat the outermost d electrons of the cations as valence electrons and the d electrons of anions are core electrons respectively (the d_{BL} approach). For GaAs, GaSb, InAs and InSb, both of these two approaches, d_{LL} and d_{BL} , are used.

In the calculation of E_m , we use the Chadi-Cohen special k -points for Brillouin zone summation. We found from the test calculations for GaAs that the difference between the $(E_m - E_v)$ -values obtained from a two-special- k -point and a ten-special- k -point calculation is only about 0.01 eV. In this paper, we therefore adopt two special k -points. The calculated results are listed in table 1 together with the $(E_h - E_v)$ -values of Harrison and Tersoff (the TB 'pinned' method). It can be seen that, although the $(E_m - E_v)$ -values are obviously different from the $(E_h - E_v)$ -values, the material dependence of these two results is perfectly consistent.

Table 1. The calculated valence band maximum energy E_v , bonding energy E_b , anti-bonding energy E_a and average bond energy E_m , together with $E_m - E_v$ obtained by the d_{LL} and d_{BL} approaches, as well as $E_h - E_v$ from the TB theory in [4].

Material	d_{LL} approach					d_{BL} approach					TB
	E_b (eV)	E_a (eV)	E_m (eV)	E_v (eV)	$E_m - E_v$ (eV)	E_b (eV)	E_a (eV)	E_m (eV)	E_v (eV)	$E_m - E_v$ (eV)	$E_h - E_v$ (eV)
Si	-5.49	5.33	-0.08	-0.13	0.05						-0.03
Ge	-6.23	4.31	-0.96	-0.57	-0.39						-0.32
AlP	-5.86	5.42	-0.22	-1.23	1.01						0.76
AlAs	-6.10	4.81	-0.65	-1.23	0.59						0.46
AlSb	-5.90	3.59	-1.16	-1.32	0.16						0.23
GaP	-6.23	5.24	-0.49	-1.13	0.64	-6.31	5.24	-0.53	-0.98	0.45	0.66
GaAs	-6.52	4.39	-1.07	-1.30	0.23	-6.59	4.48	-1.05	-1.10	0.05	0.34
GaSb	-6.21	3.40	-1.41	-1.28	-0.13	-6.26	3.52	-1.37	-1.09	-0.28	0.14
InAs	-6.52	3.61	-1.46	-1.80	0.34	-6.58	3.62	-1.48	-1.67	0.19	0.47
InSb	-6.31	2.72	-1.80	-1.87	0.07	-6.37	2.80	-1.80	-1.71	-0.09	0.28
ZnSe						-7.59	4.56	-1.51	-2.56	1.05	1.69
ZnTe						-6.96	3.62	-1.68	-2.29	0.61	1.40
CdTe						-7.27	2.83	-2.22	-2.90	0.69	1.43
HgTe						-7.41	2.78	-2.31	-2.62	0.31	

3. The aligning situation of E_m at interfaces

In the LMTO ASA band calculation of superlattices and the bulk, it is necessary to add 'empty spheres' to the most open parts in the unit cell [13, 14]. The unit cell of $(GaAs)_1(AlAs)_1(001)$ consists of $(GaAs)_1$ and $(AlAs)_1$ molecular layers. The atomic spheres and empty spheres in a $(GaAs)_1$ or $(AlAs)_1$ molecular layer correspond to those in a GaAs or AlAs unit cell in a one-to-one manner. We separate the ASA potentials obtained by self-consistent band-structure calculation of the $(GaAs)_1(AlAs)_1(001)$ superlattice into two sets which correspond to $(GaAs)_1$ and $(AlAs)_1$ molecular layers, respectively, and use them as the input of zincblende band-structure calculations (the frozen-potential approximation). In this way, the band structures and state densities of the $(GaAs)_1$ and $(AlAs)_1$ molecular layers are found. Then, the E_b -, E_a - and E_m -values are obtained from equations (1), (2) and (3), respectively. Table 2 lists these results for AlAs/GaAs, AlAs/Ge and GaAs/Ge (referred to as AB/CD below).

In table 2, it can be seen for the semiconductor pair AB/CD that the E_m -values for the bulk material AB differ from those for CD. The differences $|\Delta E_m|$

Table 2. The valence electron number Q_A , Q_B , Q_C and Q_D calculated by the dLL approach in the atomic layers of bulk materials AB, CD and molecular layers (AB)₁, (CD)₁ of (AB)₁(CD)₁ superlattices as well as the valence electron number Q , the bonding energy E_b , antibonding energy E_a and average bond energy E_m in the bulk material unit cell and in the molecular layers (AB)₁, (CD)₁ of superlattices. The Δ are results for AB-(AB)₁ and CD-(CD)₁.

AB	Q_A (electrons)	Q_B (electrons)	Q (electrons)	E_b (eV)	E_a (eV)	E_m (eV)	CD	Q_C (electrons)	Q_D (electrons)	Q (electrons)	E_b (eV)	E_a (eV)	E_m (eV)
AlAs	2.934	5.066	8.000	-6.10	4.81	-0.65	GaAs	3.122	4.878	8.000	-6.52	4.39	-1.07
(AlAs) ₁	2.937	4.972	7.909	-6.31	4.63	-0.84	(GaAs) ₁	3.119	4.971	8.091	-6.31	4.58	-0.87
Δ			-0.091			-0.19	Δ			0.091			0.20
AlAs	2.934	5.066	8.000	-6.10	4.81	-0.65	Ge	4.000	4.000	8.000	-6.23	4.31	-0.96
(AlAs) ₁	2.953	4.991	7.944	-6.36	4.73	-0.82	(GeGe) ₁	3.972	4.084	8.056	-6.13	4.42	-0.85
Δ			-0.056			-0.17	Δ			0.056			0.11
GaAs	3.122	4.878	8.000	-6.52	4.39	-1.07	Ge	4.000	4.000	8.000	-6.23	4.31	-0.96
(GaAs) ₁	3.136	4.899	8.036	-6.56	4.47	-1.04	(GeGe) ₁	3.978	3.897	7.964	-6.33	4.24	-1.04
Δ			0.035			0.03	Δ			-0.035			-0.08

are 0.42 eV, 0.31 eV and 0.11 eV, respectively. However, after they constitute a monolayer superlattice, these differences between the $(AB)_1$ and $(CD)_1$ molecular layers become 0.03 eV, 0.03 eV and 0.00 eV. It is obvious that the $|\Delta E_m|$ -values in the heterojunction AB/CD decrease by about an order of magnitude relative to those between individual semiconductors AB and CD. Therefore, the E_m -values are very close to aligned at the interface. The results are in agreement with the estimation in [4], i.e. $[E_h(B) - E_h(A)]/\epsilon_\infty$ with the long-wavelength dielectric constant $\epsilon_\infty \simeq 10$.

From the data listed in table 2, one can find that, for example, in the $(GaAs)_1(AIAs)_1(001)$ superlattice, 0.091 electrons are transferred from the higher- E_m molecular layer $(AIAs)_1$ to the lower- E_m molecular layer $(GaAs)_1$. Similarly, in $(AIAs)_1(GeGe)_1(001)$ and $(GaAs)_1(GeGe)_1(001)$, the numbers of valence electrons transferred are 0.056 and 0.035, respectively. We can consider that the valence electron transfer between two semiconductors will cause the E_m on the two sides of the heterojunction to align at this interface.

Besides the above calculations of 1 + 1 superlattices, we have performed further supercell self-consistent calculations for the 3 + 3 $(GaAs)_3(AIAs)_3(001)$ superlattice. In terms of the resulting band structure, the average bond energy E_m , the valence band maximum E_v and the valence electron number Q in each of the three $(GaAs)$ molecular layers and three $(AIAs)$ molecular layers are determined. These results are given in table 3. It is shown that the excessive number ΔQ of electrons due to interface charge transfer are almost all collected in the two interface molecular layers, namely the 3- $(GaAs)$ and 6- $(AIAs)$ layers, and the valence electron transfer is also from the molecular layer corresponding to the high- E_m bulk material $(AIAs)$ to those corresponding to the low- E_m bulk material $(GaAs)$. The excessive electron number ΔQ is consistent with those in the case of the 1 + 1 $(GaAs)_1(AIAs)_1(001)$ superlattice. In table 3 it can also be seen that the E_m -values in each molecular layer of the supercell are fairly close to each other. In particular, the difference between E_m for the two sets of interface molecular layers, i.e. 3- $(GaAs)$ and 4- $(AIAs)$, and 1- $(GaAs)$ and 6- $(AIAs)$, appears to be only 0.01 eV.

Table 3. The E_m , E_v , Q - and ΔQ -values in each of the six molecular layers of the 3 + 3 $(GaAs)_3(AIAs)_3(001)$ superlattice obtained by supercell self-consistent calculations.

Parameter (units)	Value for the following molecular layers					
	1-(GaAs)	2-(GaAs)	3-(GaAs)	4-(AIAs)	5-(AIAs)	6-(AIAs)
E_m (eV)	-0.85	-0.87	-0.89	-0.90	-0.88	-0.84
E_v (eV)	-1.10	-1.12	-1.12	-1.49	-1.48	-1.46
Q (electrons)	7.994	7.995	8.092	8.006	8.005	7.908
ΔQ (electrons)	-0.006	-0.005	0.092	0.006	0.005	-0.092

The above numerical results demonstrate directly the alignment of the E_m -level at heterojunctions. Therefore, it is reasonable to take E_m as a reference level for determining the heterojunction valence band offsets ΔE_v .

4. Results of ΔE_v and conclusions

In terms of equation (4) and the results listed in table 1, the ΔE_v -values for 16 lattice-matched heterojunctions are obtained and shown in table 4. The data listed

in the LL column are obtained from the $(E_m - E_v)$ -values listed in the d_{LL} column in table 1. The values given in the BL column are those for compounds containing Ga, In, Zn, Cd and Hg; the $(E_m - E_v)$ -values are taken from the d_{BL} column in table 1, and the rest are the same as in the d_{LL} column. The results given by several 'semiempirical methods' (CNP [1, 2], DME [3] and TB 'pinned' [4]) and self-consistent interface methods (SCIC [6] and SCSC [7]) as well as the self-consistent dipole profile (SCDP) [15] method and experiments are also listed. In this section, some of the important results will be discussed.

Table 4. The ΔE_v -values given by the d_{LL} and d_{BL} approaches (this work), the CNP [2] DME [3] and TB 'pinned' [4] methods in which reference levels were introduced, and the self-consistent interface calculation methods SCIC [6] and SCSC [7] as well as the CDSP method [15] in which the interface dipole effect was included, and experiments.

Heterojunction	ΔE_v (eV)								
	This work		Self-consistent methods			Semiempirical models			Experiment ^a [7, 8, 10]
	LL	BL	SCIC	SCSC	SCDP	DME	CNP	TB 'pinned'	
AlP/Si	0.96	0.96	1.03	0.91	0.86	0.91	0.91	0.79	
AlP/GaP	0.37	0.56	0.36	0.59	0.59	0.34	0.46	0.10	
AlAs/Ge	0.98	0.98	1.05	1.03	1.07	0.84	0.87	0.78	0.95*
AlAs/GaAs	0.36	0.54	0.37	0.53	0.54	0.39	0.55	0.12	0.55, 0.42
AlSb/GaSb	0.30	0.44	0.38	0.45		0.30	0.38	0.09	0.4
GaP/Si	0.59	0.40	0.61	0.27	0.20	0.57	0.45	0.69	0.80*
GaAs/Ge	0.62	0.44	0.63	0.46	0.45	0.45	0.32	0.66	0.56*
InAs/GaSb	0.47	0.47	0.38	0.46	0.41	0.54	0.43	0.33	0.51, 0.57
ZnSe/Ge		1.44	2.17	1.58	1.36	1.57	1.52	2.01	1.52*, 1.29
ZnSe/GaAs		1.00	1.59	1.07	0.95	1.13	1.20	1.35	1.10*, 0.96
ZnTe/GaSb		0.89		0.83	0.76	0.71	0.77	1.26	0.34* [16]
ZnTe/InAs		0.42		0.31	0.40		0.34	0.93	
ZnTe/AlSb		0.45			0.39		0.39	1.17	
CdTe/InSb		0.78		0.93	0.76	0.73	0.84	1.15	0.87*
CdTe/HgTe		0.38		0.22	0.43	0.61	0.51	0.09	0.35, 0.12
HgTe/InSb		0.40		0.45	0.26	0.01	0.33		

^a The experiments on the (110) interface are indicated with an asterisk (*). The other experiments were on the (001) interface, except for CdTe/HgTe, which was on the (111) interface.

4.1. Effects of the d state on the ΔE_v -value

From the viewpoint of the theoretical model, the present method is similar to the TB 'pinned' method of Harrison and Tersoff [4]. However, some of the important details in the calculation method are different. In fact, our results given by the LL or BL approaches (see table 4) are in excellent agreement with experimental data, whereas some of the corresponding values obtained by the TB 'pinned' method obviously deviate from the experimental values. For example, the ΔE_v -values for the common-anion heterojunctions AlP/GaP, AlAs/GaAs, AlSb/GaSb and CdTe/HgTe are much smaller. These rather smaller ΔE_v -values given by the TB 'pinned' method may be due to the omission of the d state in the TB calculations of E_v and E_h [16, 17]. In our LMTO ASA band-structure and bond energy calculations, we consider the hybridization of the d state with the s, p states. The resulting electronic structures

are, therefore, closer to those in real crystals and the E_v - and E_m -values obtained are more reasonable.

4.2. Different treatments for the d state

We found in our calculation that the resulting ΔE_v depends not only on the d states but on the different treatments for the d state. Table 5 gives the following results for GaAs obtained by the d_{LL} and d_{BL} approaches: E_v , E_m and the angular momentum decomposition of the wavefunction (the s function is zero and therefore not listed) contained in the eigenstate of the valence band maximum (Γ_{15v}). It can be found that, when the d_{LL} approach is replaced by the d_{BL} approach, the partial wave state constitution of the As atomic sphere remains unaltered, while the d partial wave of Ga decreases obviously. Together with these, the E_v -value increases by 0.2 eV, the E_m -value increases by 0.02 eV and $E_m - E_v$ decreases by 0.18 eV. Similarly, in table 1, it can also be seen that, as the d_{LL} approach is substituted for with the d_{BL} approach, the $(E_m - E_v)$ -values for GaP, GaAs, GaSb, InAs and InSb decrease by 0.15–0.19 eV. Therefore, in table 4, for AlP/GaP, AlAs/GaAs and AlSb/GaSb the ΔE_v -values (given by equation (4)) from the BL approach are larger than those from the LL approach while for GaP/Si and GaAs/Ge the BL results are smaller than the LL results

Table 5. The calculated results for E_m , E_v and angular momentum decomposition of the wavefunction at valence maximum Γ_{15v} , for GaAs.

	E_v (eV)	E_m (eV)	Ga sphere		As sphere	
			p	d	p	d
d_{LL}	-1.30	-1.07	0.13	0.09	0.69	0.01
d_{BL}	-1.10	-1.05	0.16	0.05	0.69	0.01

4.3. Comparison with other models

Recently, Lambrecht *et al* presented three theoretical models, i.e. the SCDP model [15], the self-consistent dipole model [18] and the interface-bond-polarity model [19], in which the interface dipole effect associated with interface charge transfer is investigated in detail. Their work showed that the interface dipole and dielectric screening play important roles in the energy band line-up. In several non-interface self-consistent models, e.g. the CNP, DME and TB 'pinned' models, the alignment of the reference levels E_B , E_D or E_h at interfaces is inferred from the interface dipole role or the dielectric screening effect without further strong numerical evidence. They did not demonstrate further the important role of interface charge transfer or interface dipole in detail. The present work is also a model with reference level alignment, but we perform a direct numerical test by investigating the relation between the interface charge transfer and the alignment of the average bond energy E_m . Our results demonstrate the important role of interface charge transfer in energy band line-up. The interface charge Δq introduced in the dipole model [15, 18, 19] which determines the interface dipole simply corresponds to the transferred interface charge ΔQ in the present model which causes E_m to align at interfaces. Both of these two models focus on the interface charge transfer. They differ in that, in the dipole

model, the role of charge transfer acting on energy band alignment is displayed by the charge-transfer-induced dipole whereas, in our model, it is shown by the charge-transfer-induced E_m -shift. The present method requires only calculations of the bulk material band structure and average bond energy E_m ; thus, it is more convenient than the dipole model for which the interface dipole calculations are required.

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