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The band lineups at highly strained ZnS/CdS and ZnSe/ZnTe interfaces: effects of the quadratic deformation potentials and the relaxation of the semicore d-electrons

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Abstract. The strain dependence of the band lineups at ZnS/CdS and ZnSe/ZnTe (001) interfaces has been investigated using a first principles pseudopotential planewave technique and the local density approximation for the exchange-correlation potential. Similarly, the linear and quadratic deformation potentials (DPs) of the cubic ZnS, ZnSe, ZnTe and CdS have been calculated. It is found that the ZnSe/ZnTe superlattices are of type II, with a valence band offset (Λ_v) varying almost linearly between 0.54 and 1.14 eV by going from ZnTe to ZnSe substrates. The ZnS/CdS superlattices have a very small Λ_v and show a transition from type I to type II by changing the strain state. Moreover, the conduction band offset at the ZnS/CdS interface is found to have a quite strong strain dependence. Our results for linear deformation potentials of the semiconductors considered are in the range of the available experimental data and theoretical results, and strong non-linear effects have been predicted. The quadratic DPs and the relaxation of the semicore d-electrons are found to have small, but not negligible, effects on the calculated band lineups.

1. Introduction

Strained layer superlattices (SLs) and heterostructures consisting of IIB–VI wide band gap semiconductors have received a lot of interest recently, because they are considered to be promising materials for optoelectronic devices operating in the visible light range [1]. In particular, the ZnSe/ZnTe SLs are very important for blue emitting laser diodes and semiconductor lasers [1, 2], while the ZnS/CdS quantum wells and SLs give photoluminescence (PL) emission in the UV and deep blue spectral regions [3], respectively. The cubic ZnS, ZnSe, ZnTe and CdS are direct band gap semiconductors with band gaps of 3.80, 2.80, 2.39 and 2.50 eV, respectively. Both the ZnSe/ZnTe and ZnS/CdS interfaces are highly strained with a lattice mismatch of about 7.5%. High quality SLs and quantum wells of both kinds have been successfully grown via several growth techniques. The band lineups are the key quantities in the analysis of the electronic and optical properties of these systems. Recently we have shown that the pseudopotential plane-wave (PP–PW) method with the semicore d-electrons treated as valence states yields results for the valence band offset (Λ_v) which are in excellent agreement with the direct experimental measurements, at the strained ZnS/ZnSe interface [4]. The main aim of this work is to use the same method to provide accurate theoretical results for Λ_v at the ZnSe/ZnTe and ZnS/CdS interfaces.

Despite extensive experimental and theoretical investigations, the value of Λ_v at the ZnSe/ZnTe interfaces is still not known to a satisfactory accuracy; the reported results range between 0.3 and 1.4 eV. For a recent review for Λ_v at this and some other IIB–VI/IIB–VI interfaces, see [5]. Experimentally only indirect (PL [6–8] and capacitance and current–voltage [9]) measurements have been used to determine Λ_v at this interface. The results of several theoretical investigations have also been reported, using linearized augmented plane wave (LAPW) [10], tight binding [5, 11], and PP–PW [12] methods. The results of these investigations for Λ_v between unstrained ZnSe and ZnTe (hereafter referred to by $\Lambda_{v,us}$) vary between 0.73 eV [10] to about 1.4 eV [5].

As for ZnS/CdS interfaces, the results of only two unreliable investigations for Λ_v have been reported, using a naive effective mass theory to fit the observed exciton energies of different ZnS/CdS SLs [13] and a PP–PW approach [14], which treats the semicore cations d-electrons as part of the frozen core and without including the so-called non-linear exchange-correlation core corrections (NLCCs) [15], see below. These investigations gave almost zero Λ_v.

In the indirect experimental determination of Λ_v, the strain effects are usually included via the linear deformation potential (DP) theory. Qteish and Needs [16] have found that the non-linear effects are important for lattice mismatches larger than 4%. Therefore, it is important to study the effects of the quadratic DPs on the calculated values of Λ_v at the above two highly strained interfaces. To this end we have also calculated the linear and quadratic DPs of the four involved IIB–VI compounds. We have found that the quadratic DPs are quite strong and their effects on Λ_v are small but not negligible.

The effects of the semicore d-elections on the electronic and structural properties of IIB–VI compounds and their SLs have been the subject of several investigations [17]. Qteish and Needs [18] have shown that Λ_v at the semiconductor–semiconductor interfaces involving IIB–VI compounds can be obtained with the cations semicore d-electrons treated as part of the frozen core, *provided* that the NLCCs are included. This conclusion has been reached by comparing the results obtained with those of the LMTO method, where the semicore d-electrons were considered as valence states. This is interesting since the relaxation of these d-electrons has important effects on the calculated band gaps of the IIB–VI compounds, which can be understood, using symmetry arguments, as a result of the energy shift of the upper valence band states at the Γ-point owing to the dp hybridization [19]. Therefore it would be interesting to assess more carefully the effects of the relaxation of the semicore d-electrons using the same theoretical technique. To do that, we have also calculated Λ_v at the above two interfaces using the NLCCs approach.

The calculations were performed using a first-principles PP–PW method. The computational details are the same as described in [4] for the relaxed d-electrons calculations. The differences are only in the used energy cutoffs. Here we have used 30 and 45 Ry in the calculations of the potential lineups (see section 3.2) at the ZnSe/ZnTe and ZnS/CdS interfaces, respectively. For the bandstructure calculations of CdS we used a 35 Ry energy cutoff. The Cd pseudopotential was generated by using the Kerker [20] scheme, atomic configuration $4d^{10}5s^{1.27}5p^{0.73}$ and a core radius for the d-component of 2.3 a.u. The d-component was, then, optimized by using the Lin *et al* [21] scheme. The obtained value of the wavevector cutoff is 6.15 $\sqrt{Ry}$. The transferability of the this pseudopotential has been checked and it was found to be of the same quality as that of the optimized Zn pseudopotential [21]. As for the NLCCs calculations, we used an energy cutoff of 20 Ry to extract the potential lineups, and energy cutoffs of 25 and 20 Ry, respectively, to calculate the bandstructures of the Zn-based and CdS compounds. The Zn, Cd, S, Se and Te pseudopotentials used in the NLCCs calculations were generated as described in [22].

The rest of the paper is organized as follows. In section 2 we briefly describe the effects of (001) biaxial strain on the band edges of cubic semiconductors. In section 3, we compare and discuss our results for the DPs (section 3.1) and the band lineups (section 3.2) with the available experimental data and theoretical results; section 3.3 is devoted to the effects of the quadratic DPs and the relaxation of the semicore d-electrons on the calculated values of band lineups. Finally in section 4 we summarize our main results and conclusions.

2. Effects of the strain on the band edges

The effects of the (001) biaxial strain (since we only consider one growth direction, hereafter the reference to the direction of the biaxial strain, interfaces and SLs will be suppressed) on the states at the top of the valence band and on the average band gap of cubic semiconductors are normally divided into isotropic and uniaxial contributions. The band gaps at the Γ-point, which we write as $E_c - E_{v_i}$, where i denotes the three states at the top of the valence band, are given by

$$E_c - E_{v_i} = E_{g,av} - \Delta E_{v_i}$$

where

$$E_{g,av} = E_g + \delta E_H. \tag{1}$$

Here, δE_H is the shift in the average energy band gap ($E_{g,av}$), and E_g is the energy gap at zero strain and without spin–orbit splitting. The splitting energies, ΔE_{v_i}, of the states at the top of the valence band, owing to the strain and the spin–orbit coupling, with respect to the average value are given by

$$\Delta E_{v_2} = \frac{\Delta_0}{3} - \frac{\delta E_{001}}{2}$$

$$\Delta E_{v_1} = -\frac{\Delta_0}{6} + \frac{\delta E_{001}}{4} + \frac{1}{2}\left[\Delta_0^2 + \Delta_0 \delta E_{001} + \frac{9}{4}(\delta E_{001})^2\right]^{1/2}$$

$$\Delta E_{v_3} = -\frac{\Delta_0}{6} + \frac{\delta E_{001}}{4} - \frac{1}{2}\left[\Delta_0^2 + \Delta_0 \delta E_{001} + \frac{9}{4}(\delta E_{001})^2\right]^{1/2}. \tag{2}$$

Here Δ_0 is the spin–orbit splitting and δE_{001} is the splitting of the multiplets owing to the uniaxial component of the strain. For Δ_0 we used the values 0.07, 0.43, 0.07 and 0.91 eV for ZnS, ZnSe, CdS and ZnTe, respectively, which are the same values used in [22]. The band v_2 corresponds to $|\frac{3}{2}, \frac{3}{2}\rangle$ (heavy hole) state, whereas v_1 and v_3 are mixtures of $|\frac{3}{2}, \frac{1}{2}\rangle$ (light hole) and $|\frac{1}{2}, \frac{1}{2}\rangle$ (spin–orbit split-off) states. Within the quadratic DP theory [16], δE_H and δE_{001} are related to the isotropic ($\varepsilon_{is} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$) and uniaxial ($\varepsilon_{ax} = \varepsilon_{zz} - \varepsilon_{xx}$) components of the strain by

$$\delta E_H = a\varepsilon_{is} + a_{is}\varepsilon_{is}^2 + a_{ax}\varepsilon_{is}^2 \tag{3a}$$

$$\delta E_{001} = 2b\varepsilon_{ax} + b_{ax}\varepsilon_{ax}^2 + b_{i,ax}\varepsilon_{is}\varepsilon_{ax} \tag{3b}$$

where a and b are the normal hydrostatic and axial DPs, and a_{is}, a_{ax}, b_{ax} and $b_{i,ax}$ are quadratic DPs. The ε_{xx}, ε_{yy} and ε_{zz} are the three components of the strain tensor of cubic crystal structures. $\varepsilon_{xx} = \varepsilon_{yy} = (d_\| - d)/d$ and $\varepsilon_{zz} = (d_\perp - d)/d$, where d is the equilibrium lattice parameter, $d_\|$ and $d_\perp$ are respectively the lattice parameters parallel and normal to the interface. The $d_\perp$ was determined by minimizing the strain energy via the macroscopic elasticity theory [4]. For d and the elastic constants (c_{11} and c_{12}) we used the values listed in [22], for the four considered semiconductors.

The linear and quadratic DPs were determined by using the following procedure: (i) a and a_{is} were determined from a set of bandstructure calculations for bulk semiconductors under hydrostatic pressure. (ii) b and b_{ax} were extracted from similar calculations for strained bulk semiconductors with $\varepsilon_{is} = 0$. (iii) The remaining DPs (a_{ax} and $b_{i,ax}$) were deduced from a least-squares fitting to (3) of the calculated values of δE_H and δE_{001}, for the epitaxially strained compounds and using the values of DPs determined in steps (i) and (ii).

Finally we should note that in all of our present calculations the spin–orbit splitting is taken into account *a posteriori*, by using (2). The stress-dependent spin–orbit effects have been ignored. It has been found that these effects contribute to the non-linearity on top of the valence band energies with respect to the strain configuration [23]. Therefore a more complete theory which takes into account the above effects together with the non-linear terms of δE_{001} is still lacking. The spin–orbit splitting is not implemented in our code, and so no attempts have been made to go beyond the treatment of [16].

3. Results and discussion

3.1. Deformation potentials

The DPs of ZnSe have been extracted, following the steps listed in section 2, from bandstructure calculations for this compound under both compressive and tensile biaxial stresses. Whereas only compressive biaxial stresses were considered to determine the DPs of ZnTe and CdS, and only tensile stresses were used in the case of ZnS. Therefore in the following we will discuss in details only the results obtained for ZnSe.

The calculated values of δE_H for ZnSe under compressive and tensile biaxial stresses together with the results of the least-squares fitting (3a) are shown in figure 1. The importance of the non-linear strain effects on this quantity is evident. Another important feature to note from this figure is the excellent quality of the fitting to (3a). The similarly calculated and fitted results (up to second order in ε_{is}) for δE_H of ZnSe under *isotropic* stress are also shown in figure 1. These results show that the above non-linear behaviour of δE_H is mainly the result of the last term in (3a).

The calculated values of δE_{001} for ZnSe under compressive and tensile biaxial stresses are shown in figure 2, together with the least-squares fitting to (3b). For comparison we also show the results obtained for purely *axial* ($\varepsilon_{is} = 0$) strain states. The very good quality of the least-squares fitting can be easily inferred from this figure, for all the results. This figure also shows that the effects of the last term in (3b) is quite small.

In table 1, we list our results for the linear and quadratic DPs of δE_H and δE_{001} (calculated as described above) for the cubic ZnS, ZnSe, ZnTe and CdS compounds. For comparison, the available theoretical results and experimental data are presented. The important features to note from table 1 are: (i) the linear DPs (a and b) for the Zn-based semiconductors are in satisfactory agreement with the experimental data and with other theoretical calculations; (ii) the calculated values for a are much more sensitive to the computational method used than those of b for the four considered semiconductors. The relaxation of the semicore d-electrons changes the calculated values of a, on average, by about 1 eV, while it leads to negligible changes in the calculated values of b. (iii) To the best of our knowledge, no other theoretical or experimental results for the above quadratic DPs of the IIB–VI compounds have been reported and so our present results serve as predictions.
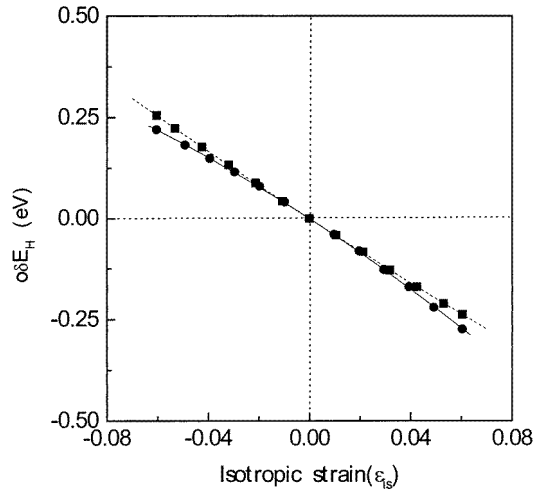
Figure 1. The change in the averaged direct bandgap of ZnSe at the Γ-point, δE_H, as a function of the biaxial strain, represented here by its isotropic component. Symbols represent calculated values and curves are the results of the fitting to (3a). The full curve and circles represent epitaxial strain configurations. The broken curve and squares represent purely isotropic strain configurations.
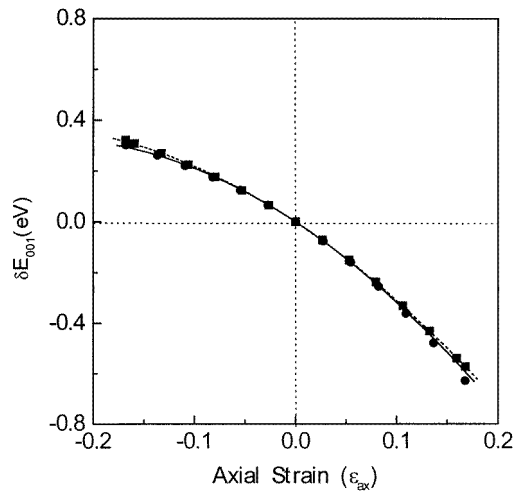

Figure 2. The splitting of the top of the valence band states of ZnSe at the Γ-point, δE_{001}, as function of the biaxial strain, represented here by its axial component. Symbols are calculated values and curves are the results of the fitting to (3b). The full curve and circles represent epitaxial strain configurations. The broken curve and squares represent purely axial strain configurations, see text.

3.2. Band lineups

The values of Λ_v at the highly strained ZnS/CdS and ZnSe/ZnTe interfaces were calculated as described in [4]. The Λ_v can be separated into two contributions: (i) the difference between the averaged total potentials (the sum of the Hartree exchange-correlation and the

Table 1. The calculated linear and quadratic DPs of ZnS, ZnSe, ZnTe and CdS under (001) biaxial strains, compared with the available theoretical and experimental data. All tabulated results are in eV.

Compound	a	a_{is}	a_{ax}	b	b_{ax}	$b_{i,ax}$
ZnTe	-4.64[a]	3.21[a]	-3.84[a]	-1.33[a]	-5.14[a]	5.30[a]
	-5.91[b]			-1.31[b]		
	-6.62[c]			-1.26[c]		
	-4.0[e]			-1.44[d]		
	-5.8[f]					
	-5.3[g]					
	-5.8[k]			-1.2[l]		
ZnSe	-4.08[a]	2.41[a]	-1.25[a]	-1.32[a]	-4.55[a]	2.13[a]
	-4.73[b]			-1.23[b]		
	-5.82[c]			-1.20[c]		
	-4.65[e]			-1.36[d]		
	-4.2[f]					
	-4.64[g]					
	-5.4[i]			-1.20[i]		
	-4.8[i]					
	-4.34[j]			-1.02[j]		
ZnS	-4.24[a]	2.33[a]	-0.62[a]	-1.18[a]	-3.26[a]	1.83[a]
	-6.95[b]			-1.25[b]		
	-6.40[c]			-1.25[c]		
	-5.64[e]			-1.39[d]		
	-4.00[f]					
	-4.53[h]					
	-4.00[i]			-0.75[i]		
	-5.00[m]					
CdS	-2.27[a]	-4.42[a]	-0.45[a]	-1.05[a]	-3.09[a]	4.03[a]
	-3.77[b]			-1.07[b]		
				-1.18[d]		

[a] Present work: relaxed d-electrons approach.
[b] [14].
[c] [38] *ab initio* pseudopotential calculations with frozen core d-electrons.
[d] [22] *ab initio* pseudopotential NLCC approach.
[e] [29] dielectric theory.
[f] [30] all-electrons potential-variation mixed-basis method.
[g] [31] LMTO calculations.
[h] [32] LMTO calculations.
[i] [33] experimental data.
[j] [34] experimental data.
[k] [35] experimental data.
[l] [36] experimental data.
[m] [37] experimental data.

local part of the ionic potentials), $\Delta \bar{V}_{tot}$, the so-called potential lineups. (ii) A bandstructure contribution which is the energy difference between the top of the valence band states of the properly strained bulk materials, calculated with $\bar{V}_{tot} = 0$, after including the effects of the spin–orbit splitting, according to (2). The $\Delta \bar{V}_{tot}$ at the ZnS/CdS and ZnSe/ZnTe interfaces were extracted from $\bar{V}_{tot}(z)$ of properly strained $(ZnS)_3/(CdS)_3$ and $(ZnSe)_3/(ZnTe)_3$ SLs, respectively. The use of such short period SLs is not surprising or new, since it has already been shown that the interface effects are usually quite short ranged [4]. It is worth noting

that Freytag [12] has concluded that at least a $(ZnSe)_4/(ZnTe)_4$ SL is required for a good convergence of $\Delta\bar{V}_{tot}$ with respect to the thickness of the ZnSe and ZnTe slabs. In our opinion the main reason for this apparent discrepancy is his use of thicker slabs (of four atoms) than the ones (of two atoms) used in our case to perform the macroscopic averaging [24] of V_{tot}. For example, we show in figure 3 the calculated $\bar{V}_{tot}(z)$ and the averaged change density, $\bar{n}(z)$, for the $(ZnSe)_2/(ZnTe)_2$ and $(ZnSe)_3/(ZnTe)_3$ SLs, lattice matched to a ZnSe substrate. For both SLs, the $\bar{V}_{tot}(z)$ and $\bar{n}(z)$ have almost constant values around the middle of the ZnSe and ZnTe slabs and the difference between the calculated values of $\Delta\bar{V}_{tot}$ in the $(ZnSe)_2/(ZnTe)_2$ and $(ZnSe)_3/(ZnTe)_3$ SLs is about 0.03 eV. This confirms the very good convergence of our results with respect to the size of the supercells used to extract $\Delta\bar{V}_{tot}$.
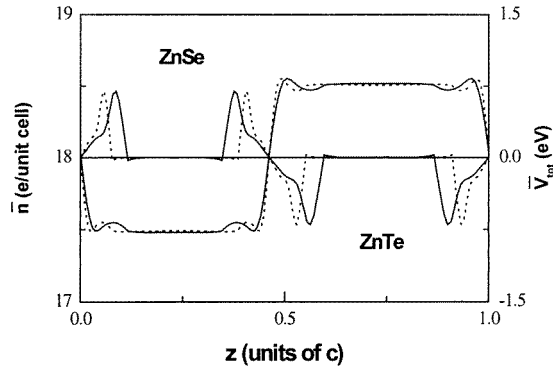

Figure 3. The averaged change density, $\bar{n}$, and total potential, $\bar{V}_{tot}$, of the $(ZnSe)_2/(ZnTe)_2$ and $(ZnSe)_3/(ZnTe)_3$ SLs, lattice matched to a ZnSe substrate. c is the length of unit cell along the growth direction.

In table 2, we list our results calculated by using the relaxed d-electrons approach for Λ_v, the averaged Λ_v (over the spin–orbit and uniaxial strain splitting), $\Lambda_{v,av}$ and the conduction band offset, Λ_c, at the ZnS/CdS and the ZnSe/ZnTe interfaces, with the three strained states considered for each of them. We also show in table 2 the values of $\Lambda_{v,us}$ for the above two interfaces. These values were obtained, at each strain state considered, from the corresponding value of $\Lambda_{v,av}$ after including: (i) the shifts in the averaged energies of the top of the valence bandstates owing to the biaxial strain of the bulk materials at the two sides of the interface; and (ii) the spin–orbit splitting. The former contribution can be calculated with the help of the absolute DPs of the top of the valence band states, a_v, of [22] (1.83, 0.92, 1.27 and -0.07 eV for ZnS, CdS, ZnSe and ZnTe, respectively). For comparison we also show in table 2 some of the other available theoretical results. The important features to note from these results are as follows.

First, the ZnSe/ZnTe SLs are of type II, with large values for Λ_v and Λ_c, with the conduction electrons and holes confined in ZnSe and ZnTe regions, respectively; whereas the Λ_v at the strained ZnS/CdS interfaces is small and changes sign by varying the strain state, at about the intermediate strain configuration. This is interesting, since it shows that the ZnS/CdS SLs experience a transition from type II (with the conduction electrons confined to the CdS and holes to the ZnS regions) to type I (both conduction electrons and holes are confined to the CdS layers) at such a strain state, by going from CdS to ZnS substrates. Previously such a transition was observed in some SLs by either varying the

Table 2. The band lineups at ZnS/CdS and ZnSe/ZnTe (001) interfaces, with the three strain configurations considered for each interface. The other available theoretical results are also shown. These band lineups are with respect to the corresponding energy state of the compound at left-hand side of the interface (for example, the positive value of Λ_v at the ZnSe/ZnTe interface implies that the top of the valence band state of ZnTe being higher in energy). All tabulated results are in eV.

			Present work		Other
					theoretical
			Relaxed		results
Interface	Substrate	Offset	d-electrons	NLCC	
ZnS/CdS	CdS	$\Lambda_{v,av}$	0.12	0.02	
		$\Lambda_{v,us}$	0.23		
		Λ_v	-0.15[a], -0.15[b], -0.27[c]	-0.26	
		Λ_c	-0.91[a], -0.91[b], -0.93[c]	-0.91	
	$Zn_{0.5}Cd_{0.5}S$	$\Lambda_{v,av}$	0.07	-0.01	0.00[d]
		$\Lambda_{v,us}$	0.15		
		Λ_v	0.02[a], 0.01[b], -0.03[c]	-0.07	
		Λ_c	-1.05[a], -1.05[b], -1.04[c]	-1.07	-0.10[d]
					-0.99[d]
	ZnS	$\Lambda_{v,av}$	0.01	-0.04	0.05[d]
		$\Lambda_{v,us}$	0.05		
		Λ_v	0.25[a], 0.24[b], 0.18[c]	0.20	0.23[d]
		Λ_c	-1.20[a], -1.20[b], -1.17[c]	-1.23	-1.05[d]
ZnSe/ZnTe	ZnTe	$\Lambda_{v,av}$	0.60	0.59	
		$\Lambda_{v,us}$	0.84		
		Λ_v	0.54[a], 0.55[b], 0.42[c]	0.52	
		Λ_c	0.63[a], 0.63[b], 0.60[c]	0.69	
	$ZnSe_{0.5}Te_{0.5}$	$\Lambda_{v,av}$	0.66	0.67	
		$\Lambda_{v,us}$	0.85		
		Λ_v	0.82[a], 0.82[b], 0.76[c]	0.83	
		Λ_c	0.66[a], 0.66[b], 0.67[c]	0.73	
	ZnSe	$\Lambda_{v,av}$	0.70	0.76	
		$\Lambda_{v,us}$	0.85		
		Λ_v	1.14[a], 1.14[b], 1.06[c]	1.20	1.15[e] 1.09[f]
		Λ_c	0.65[a], 0.65[b], 0.73[c]	0.72	0.63[e]

[a] Direct bandstructure calculations.
[b] Equation (3), using the linear and quadratic DPs listed in table 1.
[c] Equation (3), using only the linear DPs listed in table 1.
[d] [14].
[e] [10].
[f] [12].

alloying concentration at one side of the interface, as in the case of the $Zn_xMg_{1-x}Se/ZnTe$ SLs [8], or applying hydrostatic pressure, as in the case of the ZnS/ZnSe SLs [25].

Second, for both interfaces considered, the $\Lambda_{v,av}$ show a rather strong strain dependence, compared with that of ZnS/ZnSe [4] and GaAs/InAs [26] where it is found to be almost strain independent. In the case of the ZnSe/ZnTe interface, the strain variation of $\Lambda_{v,av}$ is accounted for by the DP theory and the above values of a_v for the corresponding bulk materials. For the ZnS/CdS interface, the value of $\Lambda_{v,av}$ decreases by decreasing $d_\parallel$, in contradiction with what one expects from the DP theory. The shift in $\Lambda_{v,av}$ by going

from CdS to ZnS substrates in the relaxed d-electrons and NLCCs results is of -0.11 and -0.06 eV, respectively; whereas, the corresponding shift obtained by the DP theory is 0.06 eV. The strain variation of $\Lambda_{v,av}$ at the ZnS/CdS interface is found to have important effects on the strain dependence of its Λ_c and $\Lambda_{v,us}$, see below.

Third, the Λ_c has strong (weak) strain dependence in the case of the ZnS/CdS (ZnSe/ZnTe) interface. This can be understood as follows: the Λ_c is determined according to the relation

$$\Lambda_c = E_{g,av}(R) - E_{g,av}(L) + \Lambda_{v,av} \qquad (4)$$

where R and L refer to the strained bulk materials at the right- and left-hand sides of the interface. The values of $E_{g,av}$ are calculated using (1), where for E_g we used the corresponding experimental values, averaged over the spin–orbit splitting at zero strain; for δE_H we used the self consistently calculated values of the involved semiconductor, properly strained. For the ZnSe/ZnTe interface, the change in $\Delta E_{g,av}$ by going from ZnSe to ZnTe substrates, or *vice versa*, owing to δE_H of ZnSe and ZnTe, is 0.07 eV and is almost completely compensated by the above change in $\Lambda_{v,av}$, leading to a strain independent Λ_c; whereas, in the case of the ZnS/CdS interface, the change in $\Delta E_{g,av}$ by going from, say, ZnS to CdS substrates, is quite large (0.17 eV, owing to the large difference in the values of a for ZnS and CdS, see table 1), and it has an opposite sign with respect to the corresponding change in $\Lambda_{v,av}$. This explains the strong strain dependence of Λ_c at this interface.

Fourth, our results for Λ_v at the ZnS/CdS interfaces are in very good agreement with those of Nakayama [14] obtained by using the PP–PW approach with the semicore d-electrons treated as part of the frozen core and without including the NLCCs. Such an agreement is fortuitous, since the same approach of Nakayama gave rather bad results for Λ_v at the ZnS/ZnSe interfaces compared with our results [4]. As for the ZnSe/ZnTe interfaces, our results are in excellent agreement with the LAPW results of Wei and Zunger [10].

Fifth, the calculated values of $\Lambda_{v,us}$ for the ZnSe/ZnTe (ZnS/CdS) interfaces show a very weak (quite strong) strain dependence, and an averaged value of 0.85 (about 0.15) eV. Our results for ZnSe/ZnTe is in good agreement with that of Wei and Zunger [10] of 0.73 eV, but it is considerably smaller than the results of tight-binding calculations of 1.02 eV [11] and 1.4 eV [5]. The quite strong strain dependence of $\Lambda_{v,us}$ of the ZnS/CdS interface can be understood as a consequence of the above unexpected strain dependence of $\Lambda_{v,av}$, and indicates that there are quite strong interface effects at this interface.

Direct experimental measurements for Λ_v at the strained ZnS/CdS interface are not yet available. However, Trager-Cowan *et al* [13] have found, using a naive effective mass theory approach, which uses Λ_v as an adjustable parameter, that a best fit to the exciton energies obtained by several groups using different ZnS/CdS SLs can be obtained by assuming a vanishing Λ_v. Hence the 1.30 eV difference in energy band gaps of ZnS and CdS is accommodated as Λ_c. In their work only the quantum confinement energy was considered (i.e. the strain effects on the bandstructures of bulk materials and the exciton binding energies have been neglected). They have also shown that the quantum confinement energy is insensitive to the used value of Λ_v. Therefore, their determined value of Λ_v is questionable. However, the small value of Λ_v is supported by the PL spectra of Yang *et al* [27] which show a very large blue shift (>0.5 eV), which suggests a large value of Λ_c. Our results strongly support these experimental indications, but one should keep in mind the above predicted strong strain dependence of Λ_c at this interface.

The results of several indirect experimental measurements for Λ_v at the strained ZnSe/ZnTe interface have been reported [6–9]. Unfortunately, they are scattered in the energy range between 0.3 to 1.20 eV. However, a reliable estimate has been obtained

by Rajakarunanayake *et al* [6], using a second-order $\boldsymbol{k} \cdot \boldsymbol{p}$ theory with spin–orbit and strain effects included to fit the observed PL peaks from nine different SLs. Assuming that the nature of the first PL peak is extrinsic, they found a value of 0.975 ± 0.098 eV (1.196 ± 0.134 eV in case of intrinsic PL) for Λ_v at the free-standing configuration. The former value is in good agreement with our result of 0.82 eV. The nature of the first PL peak is not yet clear, but some investigations [28] indicate that it is extrinsic and it is the result of the recombination of excitons on a single Te atom or Te clusters in the ZnSe regions. Subsequent work [7] by the same authors to fit the PL peaks of $ZnSe_xTe_{1-x}$/ZnTe SLs gave a value for $\Lambda_{v,us}$ of 0.91 ± 0.12 eV, which is also in good agreement with our corresponding result (0.85 eV). These results are further supported by the very recent PL measurements by Ferreira *et al* [8] which gave a value for $\Lambda_{v,us}$ of 0.88 ± 0.10 eV.

Finally, one may argue that significant interdiffusion occurs at the highly strained interfaces and the number of layers per each material in the corresponding coherently strained SLs is very small, which make our modelling questionable. The study of the effects of the interdiffusion on the band lineups is very interesting, and it has been found to have severe consequences on the band offsets when the interdiffused atoms are heterovalent (such as at the GaAs/ZnSe and ZnSe/Ge interfaces [39, 40]). However, the dependence of the band offsets on the interface structure becomes very weak when the interdiffusion is between isovalent atoms (such as at the GaAs/AlAs and InAs/GaSb interfaces [40, 41]), because of the lack of formation of electric dipoles at such interfaces, owing to the difference in the charge of the interdiffused ions. Therefore this may suggest that drastic effects are not expected from the interdiffusion on the band lineups at the presently considered interfaces. Further work is needed to confirm this conclusion in the case of the highly strained interfaces. As for the other point, it is well known that the interface effects are highly localized (see above), and the calculated band lineups are found to be very useful in the investigation of the electronic structure of semiconductor SLs having, even, a monolayer of one of the two compounds [42]. This justifies the usefulness of our results.

3.3. Effects of the quadratic deformation potentials and the relaxation of the semicore d-electrons on the band lineups

To study the effects of the quadratic DPs of δE_H and δE_{001} (see section 3.1) on Λ_v and Λ_c, we have also calculated these quantities using the values of $\Lambda_{v,av}$ reported in table 2 and the values of δE_H and δE_{001} calculated by using (3) and the DPs of table 1, with and without including the quadratic terms. This is done for both ZnS/CdS and ZnSe/ZnTe interfaces at the three strain states considered for each of them. The results are also listed in table 2. The important features to note from these results are: (i) the calculated Λ_v obtained by including both linear and quadratic DPs are in very good agreement with those obtained directly from the self-consistent bandstructure calculations for the properly strained bulk materials, which reflects the good quality of the least-squares fitting to (3). (ii) the effects of neglecting the quadratic DPs on Λ_v are small, but not negligible: the averaged shift (over the strain configurations considered) is about 0.1 eV for the above two interfaces. (iii) The similar shift in the value of Λ_c is very small (0.03 and 0.01 eV for the ZnSe/ZnTe and ZnS/CdS interfaces, respectively) and, thus, can be neglected.

We also list in table 2 our results for Λ_v, Λ_c and $\Lambda_{v,av}$, calculated using the NLCCs approach. By comparing our results for Λ_v obtained using the two approaches for treating the semicore d-electrons, for the two interfaces considered, we note that the NLCCs calculations give rather satisfactory band lineups. The maximum difference in the calculated values of Λ_v is 0.11 eV, in the case of a ZnS/CdS SL lattice matched to a CdS substrate. For

Λ_c, the maximum difference is 0.07 eV. Qteish and Needs [19] have already demonstrated the accuracy of the NLCCs calculations of Λ_v, by comparing their calculated values with those obtained using LMTO method, where the semicore d-electrons are treated as valence states, and with the experimental data for several III–V/II–VI and II–VI/II–VI interfaces. Our present results provide a more accurate quantitative description of the importance of the relaxation of the semicore d-electrons in the calculation of the band lineups, at least for II–VI/II–VI interfaces.

4. Conclusions

Using a first-principles pseudopotential plane-wave technique and the local density approximation for the exchange-correlation potential, we have investigated the strain dependence of the valence (Λ_v) and conduction (Λ_c) band offsets at strained ZnS/CdS and ZnSe/ZnTe interfaces. Similarly, we have calculated the linear and quadratic deformation potentials (DPs) of the shift in the averaged bandgap, δE_H, and the splitting of the top of the valence band states, δE_{001}, at the Γ-point, for the four involved bulk semiconductors. The effects of the relaxation of the cations semicore d-electrons and the quadratic DPs on the band lineups at the above two interfaces have also been studied. In the following we summarize our main results and conclusions.

(1) The ZnS/CdS SLs have small Λ_v and show a transition from type II to type I by changing the strain state, at about the intermediate strain configuration.

(2) The ZnSe/ZnTe SLs are of type II and have large Λ_v and Λ_c. The Λ_v varies between 0.54 and 1.14 eV, by going from ZnTe to ZnSe substrates, with the state at the top of the valence band in ZnTe being higher in energy.

(3) Strong non-linear behaviour has been predicted for both δE_H and δE_{001}. This behaviour is found to have small, but not negligible effects on Λ_v.

(4) The relaxation of the cations semicore d-electrons is found to be negligible in the case of the ZnSe/ZnTe interfaces, and quite small, but not negligible in the case of the ZnS/CdS interfaces. This demonstrates the reliability of the NLCC results for Λ_v at the interfaces between IIB–IV semiconductors.

(5) The averaged Λ_v (over the strain and the spin–orbit splitting), $\Lambda_{v,av}$, shows a quite strong strain dependence for both interfaces. The Λ_v and $\Lambda_{v,av}$ at only the ZnS/CdS interface show a strong strain dependence. This can be understood as a consequence of the differences between the DPs of ZnS and CdS, and the unexpected strain variation of $\Lambda_{v,av}$ of this interface.

Acknowledgment

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