Journal of Alloys and Compounds 481 (2009) 340–344

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Absence of the bowing character in the common-anion II–VI ternary alloys

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ARTICLE INFO

Article history:
Received 24 November 2008
Received in revised form 25 February 2009
Accepted 25 February 2009
Available online 14 March 2009

PACS:
71.20.Nr
71.22.+i
71.55.Gs
73.61.Ga
78.55.Et

Keywords:
II–VI semiconductors
Electronic structures
Photoluminescence

ABSTRACT

The absence of bandgap bowing in the common-anion II–VI semiconductor ternary alloys is investigated. As examples, we consider the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Zn_xSe$ alloys. The sp^3s^* tight-binding method with the inclusion of spin–orbit interactions is employed to calculate the alloy's band structure and its corresponding constituents' charge states (ionicities) as a function of composition. The variation is found to be nearly linear. The vanishingly small valence-band offset (VBO $\simeq 0$) in common-anion compounds would yield a linear scaling of bandgap energy with composition, especially as the conduction-band edge state being a singlet state with spherical symmetry. Furthermore, the two cation atoms (*Cd* and *Zn*) are found not to compete in changing their charge states as the composition is varied. The absence of such competition is believed to be the main reason for the absence of bowing. The theoretical results are compared to the available experimental data and found to be in good agreement.

1. Introduction

In the last two decades, II–VI semiconductor ternary and quaternary alloys have attracted a lot of attention because of their potential use in optoelectronic devices operating in the visible spectral range [1]. The II–VI compound semiconductors are mostly characterized by a direct bandgap with a range covering the entire visible spectrum from infrared to ultraviolet [1,2]. In addition, they are also characterized by bright emissions, which make them good candidates for applications in photonic devices.

Several theoretical and experimental investigations have focused on the properties of ternary alloys, and in particular, the *bowing* behavior of bandgap versus composition. In general, one can classify the alloys into three main classes: (i) those which possess a *bowing* character such as the common-cation $CdSe_xTe_{1-x}$ and $ZnSe_xTe_{1-x}$ alloys [3–8]; (ii) those which possess almost a linear variation of bandgap energy versus composition such as the common-anion $Cd_{1-x}Zn_xSe$ and $Cd_{1-x}Zn_xTe$ alloys [6–9]; (iii) Those which neither have the *bowing* nor the linear behaviors, such as, the metallization observed in the highly lattice mismatched nitride $IIIV_{1-x}N_x$ alloys [10–14], the negative bowing behavior seen in the alloys of $In_xGa_{1-x}As$ [15] and $GaSb_xAs_{1-x}$ [16], and the anomalous behavior in lead chalcogenides [17] where the direct gap is measured to be at the *L* point of the Brillouin zone. Nevertheless, despite decades of extensive studies, there is no commonly accepted explanation for the different characters of bandgap variation as a function of alloy composition.

On the computational side, different methods have been applied in the calculation of the band structures of II–VI semiconductor alloys. These include methods based on the dielectric two-band model [18], semi-empirical tight-binding methods [13,14,19,20], semi-empirical pseudo-potential methods [3], and self-consistent methods using local density-functional approximation (LDA) [21]. Traditionally and because of its simplicity, the virtual crystal approximation (VCA) is usually preferred for the treatment of chemical disorder in semiconductor alloys. It assumes that the atoms remain in ideal positions and completely neglects the lattice reconstruction effects. Just like the predictions of the macroscopic theory of elasticity (MTE) [22] for the case of hetero-structures [20], the VCA has proven its validity in dealing with alloys of constituents with a finite lattice mismatch (up to 7%) [23,24]. A critical analysis of the VCA validity was recently addressed by Dargam et al. [23] and by Geneste et al. [24]. The VCA usually leads to qualitative explanations of most of the features in the bandgap bowing of alloys. Unfortunately, in systems where large atomic relaxations and reconstructions take place, the VCA vastly underestimates the bandgap bowing [10,14].

In the present work, we use the sp^3s^*tight-binding (TB) method with the inclusion of spin–orbit interactions [19,20], which are important in the case of II–VI materials. The TB method has

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doi:10.1016/j.jallcom.2009.02.150

shown its reliability to successfully simulate the experimental data while incorporating the microscopic description of the material, by including the point-group symmetry of the system. Within the Slater–Koster scheme [20], the TB method uses a small basis set of atomic orbitals, and this gives the method the ability to deal with large systems, while it takes into account the band-mixing effects that are essential in the band structure of systems such as alloys. In addition to the computational task, it is worth mentioning one special and striking feature of II–VI common-anion hetero-structures, namely, the vanishingly small value of their valence-band offset (VBO). This makes the mixing of valence bands even more essential and, consequently, makes the interplay between the biaxial strain (in case of lattice-mismatched structures) and the vanishing VBO be of interest in its own right.

In another related investigation, GarcÍa et al. [25] have shown in their TB calculations on the $Zn_{1-y}Cd_ySe_{1-x}Te_x$ and $Zn_{1-y}Cd_yS_{1-x}Se_x$ quaternary alloys that the bandgap energy possesses a bowing character when only the anion mole fraction (x) is varied, while it follows almost a linear variation when only the cation mole fraction (y) is varied. Similar bowing and linear behaviors were also reported in the experimental work of Seong et al. [6] on the common-cation and common-anion II–VI *ZnTe*-based alloys. These behaviors were again corroborated in the theoretical simulations of El-Haj Hassan et al. [7,8] using the density-functional theory (DFT) and Charifi and coworkers [26] using the linearized-augmented plane wave (LAPW) method. Nonetheless, the origins of bandgap bowing or the reasons for its absence remain as open questions. This is the motivation for the present investigation which attempts to explain the presence or absence of bowing behavior in II–VI compound-semiconductor alloys especially in the case of ternary alloys, which are members of the *Cd*(*Zn*)*Se*(*Te*) family. In our recent work [27], we have applied the sp^3s^*-TB method, with the inclusion of spin–orbit coupling, to the common-cation *CdSeTe* and *ZnSeTe* ternary alloys, and have shown that they both possess the *bowing* character due to a competition between the anions (*Se* and *Te*) in trapping/losing electric charge as a function of composition. In contrast, the present work focuses on the two cases of common-anion ternary alloys $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Zn_xSe$ to investigate the complete absence of bandgap bowing. In addition, the available photoluminescence (PL) data is used to corroborate our theoretical findings.

This paper is organized as follows. The next section gives to some extent the details of the TB models and method. In Section 3, we discuss our calculated theoretical results and compare them to PL data. The last section summarizes our main findings and conclusions.

2. Computational method

Within the TB framework, atomic levels and electronic-interaction integrals are taken as adjustable parameters in order to fit the experimental or the first-principle band-structures. Vögl et al. [28] have proposed a nearest-neighbor TB description of IV and III-V semiconductors using the sp^3s^* basis set. In their work, the actual Hamiltonian is replaced with a pseudo-Hamiltonian which involves five orbitals per atom: s and 3p orbitals to describe the sp^3 hybridization and one excited s^* orbital, whose function is to provide a better description of the lower unoccupied energy levels (low-lying conduction bands (CBs)). The first extension to further incorporate the spin–orbit coupling within the TB framework was done for II–VI materials, even prior to Vögl's work, by Kobayashi et al. [19] on *CdTe* and *HgTe*. In these materials, the spin–orbit splitting is quite strong and its successful incorporation into the TB Hamiltonian has paved the way for a large field of applications, especially in the area of II–VI materials.

Moreover, in the Supercell calculations, the validity of two main points is assumed: (i) the virtual crystal approximation in evaluating the Supercell atomic structure; and (ii) the problem of energy reference between the alloy constituents is sorted out by taking the VBO into account within the scheme of VCA [14]. For instance, in the case of $Cd_{1-x}Zn_xTe$ alloy, the on-site energies of *Cd* atoms are shifted up by the VBO with respect to the ones for bulk values, whereas *Te* atoms could be bonded to *Cd* and *Zn* at the same time, and hence their on-site energies are shifted up by a weighted value of ($(1-x)$ times VBO) with respect to the ones for bulk material. We emphasize, furthermore, that the VBO used here is mosly zero in order to be consistent with the common-anion rule.

In the present work, we use the empirical TB parameters of OlguÍn and Baquero [29](shown in Table 1), which yield excellent fittings to the experimental bandgap energies and carrier effective masses. The TB Hamiltonian matrix elements are expressed in a basis of symmetrically orthonormalized atomic orbitals $|b, \mu, \mathbf{R}_i\rangle$ (the so-called Löwdin orbitals [30]), where $\mathbf{R}_I$ denotes a Bravais lattice point referring to the primitive cell; b is a basis atom in the primitive cell and μ denotes an orbital (such as $|s, (1/2)\rangle$, taken as an eigen-state of the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$) on atom b. The Hamiltonian is usually expressed [19] in terms of a basis $|b, \mu, \mathbf{k}\rangle$, which is obtained via a discrete Fourier transformation of the localized orbitals $|b, \mu, \mathbf{R}_i\rangle$, and given by

$$|b, \mu, \mathbf{k}\rangle = \frac{1}{N_w} \sum_j e^{i\mathbf{k}.\mathbf{R}_j} |b, \mu, \mathbf{R}_j\rangle. \tag{1}$$

Here $\mathbf{k}$ is a wave-vector, usually taken either from within the irreducible wedge (IW) of the Brillouin zone (BZ) if the aim is to calculate the density of states or along the high-symmetry lines if the aim is to calculate the bands, and N_w is the number of $\mathbf{k}$-vectors taken from within the IW.

With the inclusion of the spin–orbit interaction, the sp^3s^*-TB Hamiltonian is expressed in the Löwdin basis set (denoted below as $|i, \mu\rangle \equiv |b, \mu, \mathbf{R}_i\rangle$ for further simplicity) as follows:

$$H = \sum_{i,\mu} |i, \mu\rangle E_{i,\mu} \langle i, \mu| + \sum_{i,\mu;j,\nu(i \neq j)} |j, \nu\rangle U_{i\mu,j\nu} e^{i\vec{k}(\vec{r}_j - \vec{r}_i)} \langle i, \mu| \tag{2}$$

Table 1

The empirical sp^3s^* TB parameters, with the inclusion of the spin–orbit coupling, for *CdTe*, *CdSe*, *ZnSe* and *ZnTe* in units of electron-volt. The same notation as in Ref. [19] is used. The lattice constants (a_o) are in Å.

Compound	E_s^a	E_p^a	E_s^c	E_p^c	E_{s*}^a	E_{s*}^c	λ_a	λ_c
CdTe	−8.192	0.328	−0.950	6.938	10.445	6.630	0.323	0.076
CdSe	−10.167	1.034	1.080	7.646	6.027	3.962	0.143	0.067
ZnSe	−12.427	1.782	0.047	5.520	7.850	8.520	0.194	0.019
ZnTe	−9.190	0.627	−1.420	3.780	6.227	6.780	0.362	0.027

Compound	a_o	$4V_{ss}$	$4V_{xx}$	$4V_{xy}$	$4V_{sp}^{ac}$	$4V_{ps}^{ac}$	$4V_{s*p}^{ac}$	$4V_{ps*}^{ac}$
CdTe	6.48	−5.000	2.136	4.528	3.312	−3.638	2.525	−2.945
CdSe	6.05	−2.892	3.013	5.730	2.160	−5.655	2.116	−2.217
ZnSe	5.65	−6.502	3.309	5.412	1.137	−5.802	3.266	−1.870
ZnTe	6.08	−6.642	1.940	4.077	5.925	−4.673	3.827	−2.962