DENSITY FUNCTIONAL THEORY CALCULATIONS OF ELECTRONIC PROPERTIES OF CADMIUM BASED HETEROSTRUCTURES

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Abstract. Cd based semiconductor heterostructures have received great interest among the devices scientists and engineers due to their high absorption coefficients. Reliable modeling of structural and electronic properties of these semiconductors allows better prediction of their material properties in utilizing them for high performance electronic and optical device applications. In this work, we present density functional theory (DFT) to calculate the composition and strain effects on the electronic properties (e.g., band structure, density of states, bandgaps and band widths) of CdX (X=S,Se,Te) based II-VI ternary/binary heterostructures. The proposed model uses various exchange-correlation potentials (e.g., LDA, LSDA and GGA) to determine band gaps of semiconductors at Γ, L and X high symmetry points of Brillouin zone. We show that using LSDA in DFT gives better agreement with experiment for band gaps of Cd based semiconductors and their ternary alloys. Our results are also in good agreement with experiment and second nearest neighbor $sp^3s^*$ tight binding calculations.
1. Introduction

Cd based semiconductor compounds have a direct and large fundamental band gap that can be used as materials for fabricating thin film photovoltaic (PV) devices. The recent fabrication of the blue-green laser diode based on these compounds has renewed interest in their physical properties [1]. Accurate modeling of structural, electronic and optical properties of heterostructures as a function of interface strain and alloy composition is a key role to utilize ternary/binary alloys for device applications [2]. In recent years, lots of experimental and theoretical studies carried out for cadmium chalcogenides. In parallel to these researches on the fabrication processes have already made some improvement in utilizing the cadmium based alloy materials for PV device applications [2]. However, there are some theoretical issues that must be resolved before taking the full potential advantage of using cadmium compounds to make efficient photovoltaic devices. For example, qualitatively reliable simulation of electronic and optical properties of Cd based heterostructures (CdSTe/CdTe) as a function of strain and composition still need more progress for high efficient photovoltaic devices [2].

There are several theoretical methods for calculating semiconductor electronic band structure such as density functional theory (DFT), local/nonlocal empirical pseudo potential method (EPM), k.p method and semi-empirical tight binding method [3-13].

In this contribution, we present full potential linear augmented plane wave method within density functional theory (DFT) calculations to calculate the electronic band structure of zinc-blende CdS, CdSe and CdTe to investigate the effect of alloy composition and strain effects on the electronic band structure and band offsets of CdSTe/CdTe heterostructures. Bond lengths are taken as nonlinear function of composition. The model calculations are compared with those obtained by using second nearest neighbour (2NN) sp3s* tight binding model. We found that the DFT model accurately reproduces the band gaps and both the valence band and conduction band dispersion curves at high symmetry points at the edge of Brillouin zone.

2. Method of Calculation

The WIEN2K package is used in the adaptation of the partitioning the unit cell into non-overlapping atomic spheres (centered at atomic sites) and interstitial region. We have adopted sphere radii values for Cd, S, Se and Te 2.35, 2.03, 2.25 and 2.55 Bohr respectively. Self-consistent iteration is used for calculation and convergence criteria RMTKmax (where RMT is the smallest atomic sphere radius in the unit cell and Kmax is the interstitial plane wave cut-off) was set to 8.0 and also local spin density approximation (LSDA) as parameterized by Perdew and Wang [15] are used for exchange and correlation potential for the calculations. The iteration repeated until total energy converges to less than 10^-4 Ryd.

To compare our results according to the DFT by using the program package WIEN2k [14] for the electronic band structure of CdS, CdSe and CdTe, we also determined them by using 2NN sp3s* tight binding model. Conventional DFT band gaps are shifted using scissor operator [17]. The difference between the LDA (LSDA) and experimental band gap, ΔE, are scaling with high frequency dielectric constant ε∞ as ΔE = 9.1/ε∞.
Figure 1(a, b and c) shows that the comparison of electronic band structure, CdS, CdSe and CdTe calculated with the program package WIEN2k (dashed lines) and 2NN $sp^3s^*$ tight binding model (solid lines). As shown in Figure 1, comparison of WIEN2k and 2NN $sp^3s^*$ are in excellent agreement for both conduction bands and valence bands at high symmetry points.

Figure 1: Bulk band structure of CdS, CdSe and CdTe calculated by DFT (dash line) with scissor operator and 2nn sp3s* TBM.

Table 1: Calculated band gap values for CdSe, CdTe and CdS with DFT and 2nn sp3s* TB and available experiment.

<table>
<thead>
<tr>
<th>Compound</th>
<th>TB gap (eV)</th>
<th>$\varepsilon_s$ [9]</th>
<th>$9.1/\varepsilon_s$</th>
<th>Uncorrected LSDA gap (eV)</th>
<th>Corrected LSDA gap (eV)</th>
<th>Experimental Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>1.94</td>
<td>5.8</td>
<td>1.57</td>
<td>0.31</td>
<td>1.88</td>
<td>1.84 [9]</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.60</td>
<td>7.2</td>
<td>1.26</td>
<td>0.49</td>
<td>1.75</td>
<td>1.60 [17]</td>
</tr>
<tr>
<td>CdS</td>
<td>2.48</td>
<td>5.2</td>
<td>1.75</td>
<td>0.85</td>
<td>2.60</td>
<td>2.55 [17]</td>
</tr>
</tbody>
</table>
3. Composition Effects on Band Structure

Our aim is to determine the alloy composition and lattice mismatch induced interface strain effects on the band structure of Cd based heterostructures. We will first formulate the bond length of ternary semiconductors in which the effect of composition disorder is described appropriately in terms of the host bond length and the distorted bond length by the substitutional impurity without any adjustable parameter [2, 10-13]. However, detailed treatment requires the inclusion of compositional disorder effect on the structural and electronic properties of ternary alloy [2, 10-13].

Bulk CdS, CdSe and CdTe has a zinc-blende structure (space group F-43m No:216) in which the Cd atom is located at (0,0,0) and S (or Se and Te) at (0.25,0.25,0.25). We obtain the following ternary structures, CdSTe by replacing the S atoms with Te in unit cell of zinc-blende CdS. CdS(x)Te(1-x) structure for different compositions are obtained as follows. The case of 0.25 and 0.75 is obtained by replacing the S atoms at the face-center sites and apex, respectively, with Te. In this way, we obtain a cubic structure for both 0.25 and 0.75 (space group P43m, No:215). The doping of x=0.5 is obtained by replacing the S atoms at four compatible face-center sites (space group is P-4m2 No:115). The space group is tetragonal structure.

The composition variation of bulk \( A_{1-x}B_xC \) ternary alloy is written as [2,10-13]:

\[
d(x) = d_{VCA} + d_{relax} = (1-x)d_{AC}^0 + xd_{BC}^0 + x(1-x)\delta_c (d_{BC}(x) - d_{AC}(x))
\]

(3)

where \( d_{VCA} = (1-x)d_{AC}^0 + xd_{BC}^0 \) is the undistorted bond length, determined using the virtual crystal approximation (VCA) [16] and \( d_{relax} = x(1-x)\delta_c (d_{BC}(x) - d_{AC}(x)) \) is the distorted term due to cation-anion relaxation. \( d_{AC}^0 \) and \( d_{BC}^0 \) are the undistorted bond lengths of host materials AC and BC. \( d_{AC}(x) \) and \( d_{BC}(x) \) are the bond lengths of AC and BC binaries in \( A_{1-x}B_xC \) ternary:

\[
d_{BC}(x) = (1-x)d_{AC}^0 + xd_{BC}^0 + (1-x)\xi_{BC:A} (d_{BC}^0 - d_{AC}^0)
\]

(4a)

\[
d_{AC}(x) = (1-x)d_{AC}^0 + xd_{BC}^0 + x\xi_{AC:B} (d_{AC}^0 - d_{BC}^0)
\]

(4b)

where \( \xi_{BC:A} \) and \( \xi_{AC:B} \) are dimensionless relaxation parameters. \( \delta_c \) in Eq. (3) is the difference between two dimensionless relaxation parameters \( \xi_{BC:A} \) and \( \xi_{AC:B} \):

\[
\delta_c = \xi_{AC:B} - \xi_{BC:A} = \frac{1}{1 + \frac{\alpha_{AC}}{6\alpha_{BC}}(1 + 10\frac{\beta_{AC}}{\alpha_{AC}})} - \frac{1}{1 + \frac{\alpha_{BC}}{6\alpha_{AC}}(1 + 10\frac{\beta_{BC}}{\alpha_{BC}})}
\]

(5)

As we shifted bulk band gaps with scissor operator, we also shifted the ternary band gaps due to appropriate composition values as follows,

\[
e_{\infty}(CdS_xTe_{1-x}) = (1-x)e_{\infty}(CdTe) + xe_{\infty}(CdS) - x(1-x)\delta_c (e_{\infty}(CdTe) - e_{\infty}(CdS))
\]

(6)
CdSTe band gap is shifted by
\[
\Delta E \approx 9.1\varepsilon_\infty (CdS_xTe_{1-x})
\]
where \(\varepsilon_\infty\) dielectric constant, \(\delta_c\) is difference between dimensionless relaxation parameters [12] and 9.1 is a semi-empirical fitting parameter [17].

4. Results and Discussion

We used density functional theory implemented in WIEN2k package to calculate the alloy composition and strain effects on the electronic band structure of group Cd based ternary/binary semiconductor heterostructures. As an example, we introduced the composition and interface strain effects on band gaps and band offsets of \(CdS_xTe_{1-x}/CdTe\). We can calculate the composition effects on the electronic band structure of ternary/binary heterostructures using the impurity adding procedure as discussed in Section III.

We use statistical thermodynamic model [10-13] as described in detail in our previous work [2,12] to determine accurate and reliable strain effects on the electronic band structure of \(CdS_xTe_{1-x}/CdTe\) heterostructures.

![Figure 2: Predictions of composition and interface strain effects (star) calculated by 2nn sp^3s^* TBM (solid line) and DFT calculation for various composition values (x=0 0.25 0.50 0.75 1) (points) on the fundamental band gap of CdSTe/CdTe. Also we add second order polynomial fitting due to DFT calculation (black dash line) and available experimental data (red dash line).](image-url)
Figure 3: Predictions of composition and interface strain effects (dots) on the valence band offsets and band gap difference by 2nn \( sp^3s^* \) TBM and DFT calculation for various composition values (\( x = 0 \), \( 0.25 \), \( 0.50 \), \( 0.75 \), \( 1 \)) of CdSTe/CdTe.

Figure 3 shows that the interface strain on the fundamental band gap of \( CdS_xTe_{1-x}/CdTe \) heterostructure. The predicted fundamental band gap at the \( \Gamma \) point, are in excellent agreement with experimental data and also 2NN \( sp^3s^* \) tight binding model [2]. Interface strain can be quite large when the deformation potential is large as the interface strain increases with composition.

Calculating band offsets as a function of the composition and strain is an important role to determine performance of photovoltaic devices. We can calculate the composition and strain effects on band offsets across a \( A_{1-x}B_xC/BC \) ternary/binary heterointerface (e.g., \( CdS_xTe_{1-x}/CdTe \)) as follows,

\[
\Delta E_v = \left( \frac{E_v}{\Delta E_v} \right)_{ABC} - \left( \frac{E_v}{\Delta E_v} \right)_{ABC}, \quad \Delta E_{ci} = E_{ciABC} - E_{ciBC} = \Delta E_{gi} - \Delta E_v
\]

where \( E_v = E_v(\Gamma_{15}) \) is the top of the valence band at the \( \Gamma \) symmetry point, \( E_{ci} = E_{ci\Gamma}, E_{ciL}, \) and \( E_{ciX} \) are the bottom of conduction bands and \( E_{gi} = E_{gi\Gamma}, E_{giL}, \) and \( E_{giX} \) are the band gaps at the \( \Gamma, L, \) and \( X \) symmetry points are. \( \Delta E_g = E_g(ABC) - E_g(BC) \) with band gaps
$E_{\varepsilon_i}(ABC)$ and $E_{\varepsilon_i}(BC)$. $\varepsilon_{\varepsilon_i}(ABC)$ and $\varepsilon_{\varepsilon_i}(BC)$ are the optical dielectric constants of $A_{1-x}B_xC$ ternary and BC binary compounds. The calculated valance band offset is $\Delta E_{v} = 0.78$ eV at CdS/CdTe interface, in excellent agreement with 2NN $sp^3s^*$ tight binding model [12] and available experimental data [12]. Figure 4 displays the composition and strain effects on fundamental band gap difference and valence band offsets at $CdS_xTe_{1-x}/CdTe$ heterointerface. Figure 4 indicates that the interface strain effects on band gap offset in $CdS_xTe_{1-x}/CdTe$ heterostructure system can be important at high composition values when we allow increasing alloy composition the lattice mismatch increases and band gap deformation potential is large.

5. Conclusion
We have presented full potential linear augmented plane wave method to determine the alloy composition and strain effects on the electronic band structure of cadmium based ternary/binary heterostructures for photovoltaic devices. LSDA calculations shifted by scissor operator, comparing with 2NN $sp^3s^*$ tight binding model, reproduces the band dispersion curves near high symmetry points of Brillouin zone of semiconductors. The model shows good agreement with available experimental data for band gaps and band offsets. It has a key role in the design and optimization of Cd based compounds and their ternaries used for the fabrication of photovoltaic devices.

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REFERENCES