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ZB/WZ Band Offsets and Carrier Localization in CdTe Solar Cells

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ABSTRACT

Using the first-principles band-structure method, we studied systematically the stability and electronic structure of CdX ($X=S, Se, \text{ and } Te$) semiconductors with the zinc-blende (ZB) and wurtzite (WZ) crystal structures. We find that the ground-state structure of CdS is WZ, whereas for CdSe and CdTe, it is ZB. However, the total energy differences between ZB and WZ CdX are very small, less than 9 meV/2-atom. CdX in the WZ structure has a larger band gap than the one in the ZB structure. The band alignment on the ZB/WZ interface is type-II, with holes localized on the WZ side and electrons on the ZB side. The predicted carrier localization in a mixed ZB/WZ system can significantly affect device transport properties.

1. Introduction

Unlike most III-V and II-VI semiconductors, CdX ($X=S, Se, \text{ and } Te$) compounds exist in both ZB and WZ structures or in mixed ZB/WZ phases [1]. Depending on the growth condition, one can stabilize one of the two crystal structures either by epitaxial strain on proper substrates or buffer layers, or by controlling the growth temperature. Understanding the effects of this additional structure freedom in CdX is important for making more efficient and reliable solar cells. In this work, we systematically study the stability and electronic structure of Cd II-VI compounds in both ZB and WZ phases and at the ZB/WZ interfaces using the first-principles band-structure method based on the local density approximation (LDA) [2]. We calculated (a) the equilibrium crystal structures of ZB and WZ CdX semiconductors, (b) the band offsets at the ZB/WZ interface for these Cd compounds, (c) the valence-band splitting at the top of the valence band of WZ CdX, and (d) the carrier localization of valence-band maximum (VBM) and the conduction-band minimum (CBM) states in mixed ZB/WZ systems. In the following, we describe the method of our calculation and discuss the significant physics of the results.

2. Method of Calculations

The band structure and total energy calculations are performed using the LDA, as implemented by the full-potential linearized augmented plane wave (LAPW) method [2]. Large numbers of k points for the Brillouin-zone integration and high cut-off energies for the basis functions are used to ensure that the total energy differences between the WZ and ZB phases are converged to within 1 meV/2-atom. All the structural parameters are fully relaxed to minimize the total energy. The band structures are calculated at their respective equilibrium lattice constants [3].

The valence-band offsets $\Delta E_v(\text{ZB/WZ})$ for compounds CdX are calculated using the standard approach similar to the

photoemission measurement [4]. In this approach, the valence-band offset is given by

$$\Delta E_v(\text{ZB/WZ}) = \Delta E_{\text{VBM},C}(\text{WZ}) - \Delta E_{\text{VBM},C}(\text{ZB}) + \Delta E_{C,C'} \quad (1)$$

Here, $\Delta E_{\text{VBM},C}(\text{WZ}) = E_{\text{VBM}}(\text{WZ}) - E_C(\text{WZ})$ is the core-level to valence-band maximum energy separations for CdX in the WZ structure, and $\Delta E_{C,C'} = E_C(\text{WZ}) - E_C(\text{ZB})$ is the difference in core-level binding energy between CdX in each side of the ZB/WZ interface. We find that, even though the ZB and WZ structures have very similar volumes and local structures, the core-level difference $\Delta E_{C,C'}$ makes a significant contribution to Eq. (1). Thus, it is necessary not only to calculate the bulk CdX in the ZB and WZ phases, but also, to calculate the core-state alignment across the ZB/WZ interface. The conduction-band offsets can be obtained by using the relation $\Delta E_c = \Delta E_g + \Delta E_v$, where ΔE_g is the band-gap difference between the WZ and ZB phases.

3. Results

Although the ZB structure has the cubic space group and the WZ structure has the hexagonal space group, the two structures are in fact very similar; they start to differ only in their third-nearest-neighbor atomic arrangement. Our calculation [3] showed that for CdX in the WZ structure, the calculated c/a ratios and the internal structure parameters u are very close to the ideal values of $c/a=1.633$ and $u=0.375$, respectively. Thus, the total energies and the direct band gaps at the Γ point for ZB and WZ CdX are expected to be similar [5]. Table I gives the calculated total-energy differences $\Delta E(\text{ZB/WZ})$, band-gap differences $\Delta E_g(\text{ZB/WZ})$, valence-band and conduction-band offsets $\Delta E_v(\text{ZB/WZ})$ and $\Delta E_c(\text{ZB/WZ})$ between ZB and WZ CdX compounds, and the valence-band splitting $\Delta E_{\text{AB}}(\text{WZ})$. We find the following results:

(a) $\Delta E(\text{ZB/WZ})$ is negative for CdS, but positive for CdSe and CdTe. These results indicate that at low temperatures CdS is stable in the wurtzite structure, whereas CdSe and CdTe are stable in the zinc-blende structure. However, the total energy differences between the WZ and ZB structures are very small. They are -2, 2, and 9 meV/2-atom. The increase of $\Delta E(\text{ZB/WZ})$ as anion atomic number increases from S to Se to Te is consistent with the fact that as anion atomic number decreases, the compound becomes more ionic, thus stabilizing the WZ structure which has a larger Madelung constant than the ZB structure.

Due to the small energy differences between the ZB and WZ phases, the actual crystal structure of Cd compounds is highly dependent on the substrate orientation, growth temperature, and history of annealing. As a test, we calculated the total energy difference $\Delta E(\text{ZB/WZ})$ of CdTe strained on a

Table I. Calculated total energy differences $\Delta E(\text{ZB/WZ})$ (in meV/2-atom), band-gap differences $\Delta E_g(\text{ZB/WZ})$, band offsets $\Delta E_v(\text{ZB/WZ})$ and $\Delta E_c(\text{ZB/WZ})$ and the valence-band splitting ΔE_{AB} in the WZ (all in meV).

| Properties | CdS | CdSe | CdTe |
|----------------------------|-----|------|------|
| $\Delta E(\text{ZB/WZ})$ | -2 | 2 | 9 |
| $\Delta E_g(\text{ZB/WZ})$ | 69 | 59 | 47 |
| $\Delta E_v(\text{ZB/WZ})$ | 46 | 35 | 18 |
| $\Delta E_c(\text{ZB/WZ})$ | 115 | 94 | 65 |
| ΔE_{AB} | 18 | 33 | 53 |

WZ CdS (0001) substrate. In this calculation, the lattice constants in the plane are fixed to the one for equilibrium bulk CdS, while the lattice constant perpendicular to the substrate is free to relax. We find that $\Delta E(\text{ZB/WZ})$ is reduced from 9 meV/2-atom for bulk CdTe to zero for the epitaxial CdTe, suggesting that epitaxial CdTe can form more easily in the WZ structure than bulk CdTe can.

(b) The band gaps of the WZ structure are 69, 59, and 47 meV larger than those in the ZB structure for CdS, CdSe, and CdTe, respectively. The increase of the band gap in the WZ structure is due to lower symmetry in the WZ structure, which results in a coupling between the CBM Γ_{1c} state and the splitting VBM Γ_{1v} state [5]. The level repulsion between these two states leads to an upward shift of the CBM, thus, increasing the band gap of the WZ structure. The level repulsion also contributes to the crystal-field splittings at the VBM.

(c) The calculated valence-band splittings $\Delta E_{AB}(\text{WZ})$ between the Γ_{9v} (A) and the Γ_{7v} (B) states are 18, 33, and 53 meV for CdS, CdSe, and CdTe, respectively. The increase of $\Delta E_{AB}(\text{WZ})$ as anion atomic number increases can be explained by the fact that as anion atomic number increases, the band gap decreases; thus, the coupling between the CBM and the Γ_{7v} (B) state becomes larger, pushing the Γ_{7v} (B) state down. Our LDA calculated results can be compared with experimental values [1] of 15 and 25 meV for CdS and CdSe, respectively. It shows that LDA overestimate the splittings by about 25%, consistent with the LDA underestimation of the band gaps.

(d) Due to the crystal-field splitting in the WZ structure, the VBM of the WZ structure is higher than the VBM of the ZB structure. The calculated valence-band offsets between the ZB and WZ structures are 46, 35, and 18 meV, respectively, for CdS, CdSe, and CdTe, decreasing as anion atomic number increases. Using the calculated band-gap differences $\Delta E_g(\text{ZB/WZ})$, the conduction-band offsets are 115, 94, and 65 meV, respectively, for CdS, CdSe, and CdTe. The CBM on the WZ side is higher. This type-II band alignment indicates that in a sample with mixed ZB and WZ phases, the hole state will localize on the WZ region, whereas the electron state will localize in the ZB region. The charge localization will be more significant for the VBM state because the hole effective mass is much larger than the electron effective mass. The degree of the carrier localization decreases as the anion atomic number increases, because $\Delta E_v(\text{ZB/WZ})$ and $\Delta E_c(\text{ZB/WZ})$ decrease from CdS to CdSe to CdTe. These expectations are confirmed

[3] by examining our calculated plane-averaged charge distribution of the VBM and CBM of $(\text{ZB})_6/(\text{WZ})_6$ superlattice for CdS, CdSe and CdTe.

The predicted band alignment and carrier localization in a mixed ZB/WZ system are expected to have significant effects on the electronic and transport properties of Cd compounds and the affect their device applications. For example, in a p-CdTe/n-CdS solar cell, formation of a thin-layer WZ CdTe on the WZ CdS substrate (Fig. 1) can reduce the minority-carriers (electrons in CdTe and holes in CdS) collection, thus reducing the cell efficiency. This is because WZ CdTe has a higher VBM than ZB CdTe. Thus, holes generated in CdS will be trapped in WZ CdTe before they can be collected by ZB CdTe. On the other hand, ZB CdTe has a lower CBM than WZ CdTe. The electrons have to overcome an unfavorable spike before they can be collected by CdS. The effect of minority-carrier trapping will be even larger if the

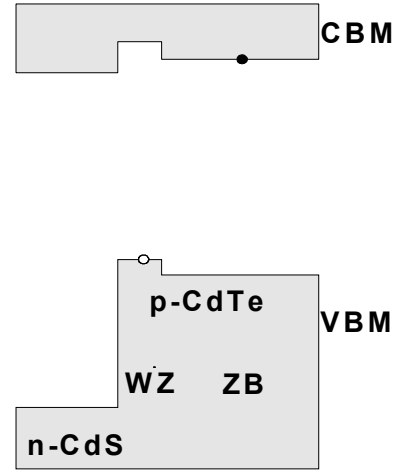


Fig. 1. Schematic plot of the band alignment at the n-CdS/p-CdTe interface.

WZ CdTe near the interface is strained on the WZ CdS substrate because the epitaxial strain will move up the VBM of WZ CdTe by 0.53 eV and the CBM by 0.30 eV, thus enhancing the energy barriers (Fig. 1).

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