

Structure stability and carrier localization in CdX ($X=S, Se, Te$) semiconductors

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We studied systematically the structural and electronic properties of binary CdX ($X=S, Se, \text{ and } Te$) semiconductors in both zinc-blende (ZB) and wurtzite (WZ) structures, the band alignment on the ZB/WZ interfaces, and carrier localization induced by the band offsets. We show, by first-principles band-structure calculation that at low temperature, CdS is stable in the wurtzite structure, while CdSe and CdTe are stable in the zinc-blende structure. However, coherent substrate strain can change CdTe to be more stable in the wurtzite form. We find that CdX in the wurtzite structure has a larger band gap than the one in the zinc-blende structure. The band alignment on the ZB/WZ interface is found to be type II with holes localized on the wurtzite side and electrons on the zinc-blende side.

Cd-based II–VI semiconductor compounds are of considerable interest due to their applications in optoelectronic devices.^{1,2} Unlike most III–V and II–VI semiconductors, CdX ($X=S, Se, \text{ and } Te$) compounds exist in both zinc-blende (ZB) and wurtzite (WZ) structures or in mixed (ZB)/(WZ) phases.³ 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. This additional structure freedom provides an opportunity for making more efficient and reliable devices by choosing the appropriate polytypism of the compounds. For example, it was shown⁴ that extended defects in wurtzite material tend to stay in the basal plane. Thus, when grown along the [0001] direction, defects propagation tends to be suppressed, leading to improved device stability. Wurtzite compounds also present a natural splitting between the heavy-hole and light-hole band, thus, like ordered semiconductor alloys and superlattices, they can be used as high-quality spin-polarized photoelectron sources.⁵ Another interesting phenomenon is that in making CdTe/CdS solar cells, the wurtzite structure is often observed when CdTe is grown on a hexagonal CdS substrate.⁶ It is not clear how the existence of the wurtzite CdTe affects the carrier distribution and device performance in this system.

In this paper we study systematically the electronic structures of Cd-based compounds in both zinc-blende and wurtzite structures and ZB/WZ interfaces using first-principles, self-consistent electronic structure theory based on the local-density approximation (LDA). We have calculated (a) the equilibrium crystal structures of zinc-blende and wurtzite Cd-based 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 wurtzite CdX, and (d) carrier localization in valence-band maximum (VBM) and conduction-band minimum (CBM) states at interfaces of mixed ZB/WZ systems. This paper describes the salient features of these calculations and discusses the significant physics of the results.

The band structure and total-energy calculations are performed using the first-principles density-functional formalism as implemented by the general potential, all electron, relativistic, linearized augmented plane wave (LAPW)

method.⁷ The Cd 4*d* electrons are treated in the same footing as the other valence states. No shape approximations are employed for either the potential or the charge density. We used the Ceperley-Alder exchange correlation potential⁸ as parameterized by Perdew and Zunger.⁹ The Brillouin-zone integration of the superstructures is performed using the Monkhost-Pack special \mathbf{k} points scheme.¹⁰ A large number of k points and high-cutoff energies for the basis functions are used to ensure that the total-energy difference between the wurtzite and ZB phases are converged to within 1 meV/2 atom. All the structural parameters are fully relaxed to minimize the total energy.

The valence-band offsets ΔE_v^{WZ-ZB} for compounds CdX are calculated using the standard approach.^{11,12} In this approach, the valence-band offset is given by

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

Here, $\Delta E_{VBM,C}^{WZ} = E_{VBM}^{WZ} - E_C^{WZ}$ is the core level to valence-band maximum energy separation for CdX in the wurtzite structure and $\Delta E_{C,C'} = E_C^{WZ} - E_{C'}^{ZB}$ is the difference in core-level binding energy between CdX on each side of the ZB/WZ interface. We find that, even though the zinc-blende and wurtzite structures have very similar volume and local structure, 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 zinc-blende and wurtzite phases, but also to calculate the core state alignment across the ZB/WZ interface (see below). The conduction-band offsets are obtained by using the relation $\Delta E_c^{WZ-ZB} = \Delta E_g^{WZ-ZB} + \Delta E_v^{WZ-ZB}$.

While the zinc-blende structure has the cubic space group and the wurtzite 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. In an ideal wurtzite structure one finds $a_{WZ} = a_{ZB}/\sqrt{2}$, $(c/a)_{WZ} = \sqrt{8/3} = 1.633$, and the internal structure parameters $u_{WZ} = 0.375$. For a real wurtzite compound, due to the lower crystal symmetry, the structural parameters could differ from these ideal values. Thus, a wurtzite compound can have two types of distinct cation-anion nearest neighbor bond lengths.

TABLE I. Calculated structural parameters a , c , and u , and bulk moduli B for zinc-blende and wurtzite CdS, CdSe and CdTe. Results are compared with experimental values (Ref. 3).

Properties	CdS		CdSe		CdTe	
	LDA	Exp.	LDA	Exp.	LDA	Exp.
a_{ZB} (Å)	5.7958	5.818	6.0412	6.052	6.4400	6.482
a_{WZ} (Å)	4.1009	4.136	4.2717	4.300	4.5499	
c_{WZ} (Å)	6.6866	6.714	6.9786	7.011	7.4512	
$(c/a)_{WZ}$	1.6305	1.623	1.6336	1.630	1.6377	
u_{WZ}	0.3757		0.3756		0.3754	
B_{ZB} (kbar)	703		592		466	445
B_{WZ} (kbar)	692	620	579	530	454	

One bond, parallel to the (0001) direction, has length R_1 , and the other three bonds have equal lengths R_2 . They are given by

$$R_1 = uc,$$

$$R_2 = \sqrt{1/3 + (1/2 - u)^2 (c/a)^2} a. \quad (2)$$

Table I gives our calculated lattice parameters a and c , internal structure parameters u , and bulk moduli B for CdS, CdSe, and CdTe in both zinc-blende and wurtzite phases. We have the following results:

(i) the calculated lattice parameters a are within 0.7% of the experimental values.³ For the wurtzite structure, the calculated c/a ratios are 1.631, 1.634, and 1.638, for CdS, CdSe and CdTe, respectively, very close to the ideal value $c/a = 1.633$.

(ii) The calculated internal structure parameters u are 0.3757, 0.3756, and 0.3754 for CdS, CdSe, and CdTe, respectively, very close to the ideal value $u = 0.375$. These results suggest that the splittings of Cd-anion nearest neighbor bond lengths in the wurtzite structure are very small. The slight decrease in the u parameter is consistent with the slight increases of the c/a ratio as anion atomic number increases. This is because in wurtzite semiconductors, due to the competition between bond-bending and bond-stretching forces, the c/a ratio and the u parameter always move in the opposite directions,¹³ similar to that found for zinc-blende semiconductors with (111) trigonal distortion.¹⁴

(iii) The calculated bulk moduli are in good agreement with experimental data.³ They decrease as the anion atomic number increases. The slightly larger calculated bulk moduli relative to the experimental data are due partly to the underestimation of the lattice constants (the calculated bulk moduli at experimental lattice constants are 664, 577, and 423 kbar, for zinc-blende CdS, CdSe, and CdTe, respectively). The bulk moduli for the WZ structure is predicted to be slightly smaller than their zinc-blende counterparts.

With the subtle differences between the zinc-blende and the wurtzite structures, the total energies and the direct band gaps at the Γ point are expected to be similar for these two structures. Table II gives the calculated total-energy differences ΔE^{WZ-ZB} , band-gap differences ΔE_g^{WZ-ZB} , valence-band and conduction-band offsets ΔE_v^{WZ-ZB} and ΔE_c^{WZ-ZB} ,

respectively, between binary zinc-blende and wurtzite compounds, and the valence-band splitting ΔE_{AB}^{WZ} . We find the following results:

(a) ΔE^{WZ-ZB} is negative for CdS, while positive for CdSe and CdTe. These results indicate that at low temperature CdS is stable in the wurtzite structure, while CdSe and CdTe are stable in the zinc-blende structure. However, the total-energy differences between the wurtzite and zinc-blende structures are very small. They are -2 , 2 , and 9 meV/2 atom for CdS, CdSe, and CdTe, respectively. The increase of ΔE^{WZ-ZB} as the anion atomic number increases from S to Se to Te is consistent with the fact that as the anion atomic number decreases the compound becomes more ionic. Since the Madelung constant for the wurtzite structure ($\alpha_M^{WZ} = 1.6413$) is slightly larger than the zinc-blende structure ($\alpha_M^{ZB} = 1.6381$), the more ionic the compound is, the more likely the compound will have the wurtzite ground-state structure. For CdS and CdSe, our calculated results of -2 and 2 meV/2 atom are similar to the results of Yeh *et al.*,¹⁵ found to be -2 and 3 meV/2 atom. However, our results do not agree with the calculated results of Murayama and Nakayama¹⁶ of -9 and -2 meV/2 atom for CdS and CdSe, respectively. Their results would suggest that at low temperature CdSe are stable in the wurtzite structure. This is in contradiction with experimental observation,¹⁷ where the low-temperature stable phase for CdSe is found to be zinc-blende and CdSe transforms into the wurtzite structure at about 95°C .

Due to the small energy differences between the zinc-blende and wurtzite phases, the actual crystal structure of Cd compounds will depend sensitively on the substrate orientation, growth temperature, and history of annealing. As a test, we calculated the total-energy difference ΔE^{WZ-ZB} of CdTe strained on a wurtzite CdS (0001) substrate. In this calculation

TABLE II. Calculated total-energy differences ΔE^{WZ-ZB} , band-gap differences ΔE_g^{WZ-ZB} and band offsets ΔE_v^{WZ-ZB} and ΔE_c^{WZ-ZB} between Cd-based zinc-blende and wurtzite compounds. The calculated valence-band splittings ΔE_{AB} in the wurtzite structure are also given.

Properties	CdS	CdSe	CdTe
ΔE^{WZ-ZB} (meV/2 atom)	-2	2	9
ΔE_g^{WZ-ZB} (meV)	69	59	47
ΔE_v^{WZ-ZB} (meV)	46	35	18
ΔE_c^{WZ-ZB} (meV)	115	94	65
ΔE_{AB}^{WZ} (meV)	18	33	53

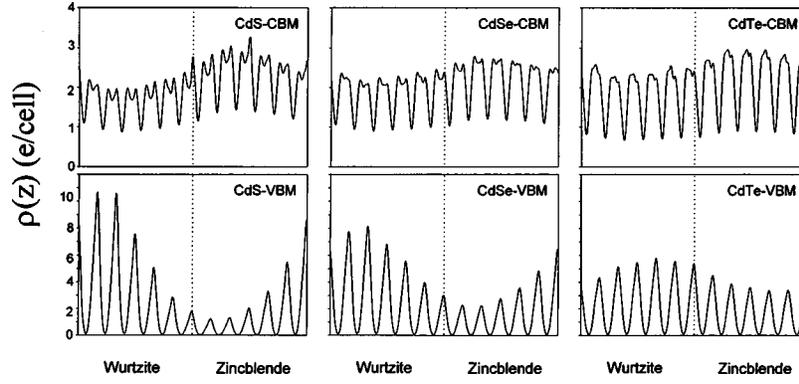


FIG. 1. Plane averaged charge densities of CBM and VBM states of $(WZ)_6/(ZB)_6$ superlattices for CdS, CdSe, and CdTe. We see that VBM is more localized on WZ side while CBM is more localized on zinc-blende side.

tion the lattice constants in the plane are fixed to be the one for equilibrium bulk CdS, while the lattice constant perpendicular to the substrate is free to relax. We find that ΔE^{WZ-ZB} 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 wurtzite structure than bulk CdTe can. This reduction in ΔE^{WZ-ZB} is attributed to the fact that wurtzite CdTe is slightly more soft and can relax more efficiently in the $[0001]$ direction.

(b) The band gaps of the wurtzite structure are 69, 59, and 47 meV larger than that in the zinc-blende structure. The reason for this increase of the band gap in the wurtzite structure is as follows:¹⁸ Both the zinc-blende and wurtzite structures can be considered as layered along the $[111]$ or the $[0001]$ direction. They differ only in their stacking sequences. Consequently, electron states on the $\bar{\Gamma}-\bar{A}$ line of the wurtzite Brillouin zone are derived directly from the one on the zinc-blende $\Gamma-L^{111}$ line. In particular, at the $\bar{\Gamma}$ point, we have

$$\bar{\Gamma}_1 \rightarrow \bar{\Gamma}_1(\Gamma_1); \quad \Gamma_{15} \rightarrow \bar{\Gamma}_1(\Gamma_{15}) + \bar{\Gamma}_6(\Gamma_{15}). \quad (3)$$

Here, we denote wurtzite states by an overbar and indicate in parentheses the parent zinc-blende states. The states of the same symmetry in the wurtzite structure can interact and thus repel each other with magnitude that in perturbation theory is inversely proportional to their initial energy difference and directly proportional to the square of their coupling matrix element ΔV^2 . Therefore, the coupling between the $\bar{\Gamma}_{1v}(\Gamma_{15v})$ and $\bar{\Gamma}_{1c}(\Gamma_{1c})$ states lead to an upward shift of the CBM $\bar{\Gamma}_{1c}(\Gamma_{1c})$ state, thus increasing the band gap of the wurtzite structure. It also contributes to the crystal-field splitting at the VBM between the $\bar{\Gamma}_{6v}(\Gamma_{15v})$ and the $\bar{\Gamma}_{1v}(\Gamma_{15v})$ states.

(c) After including the spin-orbit coupling, the calculated valence-band splittings ΔE_{AB}^{WZ} between the $\bar{\Gamma}_{9v}(A)$ and $\Gamma_{7v}(B)$ are 18, 33, and 53 meV, for CdS, CdSe, and CdTe, respectively. The increase of ΔE_{AB}^{WZ} as the anion atomic number increases can be explained by the fact that as the anion atomic number increases, the band gap decreases, thus the coupling between the $\bar{\Gamma}_{1v}(\Gamma_{15v})$ and $\bar{\Gamma}_{1c}(\Gamma_{1c})$ states becomes larger, pushing the $\bar{\Gamma}_{1v}$ state down. Our LDA calculated results can be compared with experimental values³ of 15 and 25 meV for CdS and CdSe, respectively. It shows that

LDA overestimate the splittings by 20 to 30%, consistent with the underestimation of the LDA band gaps. Similar results have been found for ordered III-V semiconductors alloys.¹⁹

(d) Due to the crystal-field splitting in the wurtzite structure, the VBM of the wurtzite structure is higher than the VBM of the zinc-blende structure. The calculated valence-band offsets between the zinc-blende and wurtzite structures are 46, 35, and 18 meV, respectively, for CdS, CdSe, and CdTe, decreasing as anion atomic number increases. The conduction-band offsets can be obtained using the relation $\Delta E_c^{WZ-ZB} = \Delta E_g^{WZ-ZB} + \Delta E_v^{WZ-ZB}$, which gives ΔE_c^{WZ-ZB} to be 115, 94, and 65 meV, respectively, for CdS, CdSe, and CdTe. The CBM on the wurtzite side is higher. This type-II band alignment indicates that in a sample with mixed zinc-blende and wurtzite phases, the hole state will localize in the wurtzite region while the electron state will localize in the ZB region. To test this, we calculated electronic structures of $(ZB)_n/(WZ)_n$ superlattices. Figure 1 plots the calculated plane averaged charge distribution of the VBM and CBM states of the $(ZB)_6/(WZ)_6$ superlattice for CdS, CdSe, and CdTe. We see that, indeed, the VBM state is more localized in the wurtzite region, while the CBM is more localized in the zinc-blende region. The charge localization is more significant for the VBM state since the hole effective mass is much larger than the electron effective mass (despite ΔE_c^{WZ-ZB} being larger than ΔE_v^{WZ-ZB}). The degree of the carrier localization decreases as anion atomic number increases, consistent with our prediction that ΔE_v^{WZ-ZB} and ΔE_c^{WZ-ZB} decrease from CdS to CdSe to CdTe.

Murayama and Nakayama¹⁶ have calculated ΔE_v^{WZ-ZB} for the three Cd compounds using a pseudopotential method. They found that ΔE_v^{WZ-ZB} are 19, 30, and 21 meV, respectively, for CdS, CdSe, and CdTe. However, in their calculation they assumed that no dipole potential exists across the interface, thus ΔE_v^{WZ-ZB} is determined only by the first two terms on the right-hand side of Eq. (1), i.e., they were determined purely from the binary calculations. We found that this assumption is not justified. Without the third term in Eq. (1), our calculated ΔE_v^{WZ-ZB} are only $-1, 3,$ and 10 meV, for CdS, CdSe, and CdTe, respectively. It is not surprising to see that the interface term in Eq. (1) plays the most important roles in determining ΔE_v^{WZ-ZB} for the more ionic compounds CdS and CdSe, since wurtzite compounds are polar and piezoelectric.

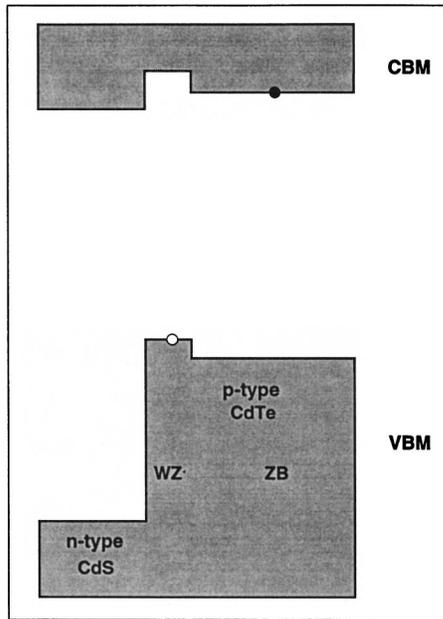


FIG. 2. Schematic plot of the band alignment at the n -CdS/ p -CdTe interface. We see that electron is trapped on zinc-blende CdTe while holes are trapped on wurtzite CdTe, thus reducing the minority-carrier collections.

This 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 affect their device applications. For example, in

a p -CdTe/ n -CdS solar cell, formation of a thin layer of wurtzite CdTe on the wurtzite CdS substrate (Fig. 2) can reduce the minority carriers (electrons in CdTe and holes in CdS) collection, thus reducing the cell efficiency. This is because wurtzite CdTe has a higher VBM than zinc-blende CdTe, thus holes generated in CdS will be trapped in wurtzite CdTe before they can be collected by zinc-blende CdTe. On the other hand, zinc-blende CdTe has a lower CBM than wurtzite CdTe; the electrons have to overcome an unfavorable spike before it can be collected by CdS. The effect will be even larger if the wurtzite CdTe near the interface is strained on the wurtzite CdS substrate, because the epitaxial strain will move up the VBM of CdTe by 0.53 eV and the CBM by 0.30 eV, enhancing the energy barriers.

In summary, we have studied systematically the electronic properties of Cd-based compounds and interfaces using the first-principles band-structure method. We find that wurtzite CdX have nearly ideal structural parameters. The total-energy differences ΔE^{WZ-ZB} are very small, thus, the actual crystal structures of the Cd compounds at room temperature will depend sensitively on their growth conditions. The band gaps of wurtzite Cd compounds are larger than their zinc-blende counterparts. The VBM of wurtzite CdX is higher than the VBM of zinc-blende CdX; this leads to carrier localization in a mixed ZB/WZ system and can affect significantly device transport properties.

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