Ab initio electronic band structure study of the valence bands of II–VI $C(2 \times 2)$ reconstructed surfaces

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Abstract. The structural and electronic properties of CdTe(001), CdSe(001), and ZnSe(001) $C(2 \times 2)$ reconstructed surfaces have been investigated through the use of first-principles calculations. To simulate the surface, we employed the slab model. Using the experimentally determined lattice parameters as inputs, we relaxed the internal atomic positions of the outer atomic layers. We demonstrate that our model appropriately reproduces both the surface structural parameters and the known electronic properties found for these semiconductor compounds in bulk. Finally, we discuss our results of the projected bulk bands and the surface and resonance states found for these surfaces.

1. Introduction

Type II–VI semiconductors have continued to receive increasing attention because of their applications in optoelectronic devices for detecting and stimulating emission in the IR (mainly CdHgTe) and blue spectral regions (ZnSe). In this context, CdTe is used as a buffer for the growth of Cd$_x$Hg$_{1-x}$Te heterostructures. The (001) surfaces of II–VI compounds exhibit different reconstructions as functions of temperature and the growth conditions [1, 2, 3, 4, 5]. Knowledge of the atomic structures of these surfaces is crucial for understanding the energy band structure and, consequently, for the tailoring of heterostructures with desired electronic properties. The CdTe(001) surface was experimentally studied in early works [1, 6, 7]. From the theoretical perspective, this system has been studied using an empirical approach [8, 9, 10] and using first-principles calculations [11, 12]. Recently, a DFT study for CdSe(001) was conducted [13]. Furthermore, ZnSe(001) has also been the focus of extensive studies in the literature [3, 14, 15].

To contribute to the understanding of the electronic properties of the II–VI surface compounds, in this paper, we report a study on the CdTe(001) – $C(2 \times 2)$ reconstructed surfaces. For this purpose, a slab that included seventeen atomic layers and a vacuum of four atomic layers was constructed. The top view and side view of the (001) $C(2 \times 2)$ reconstructed surface is schematically illustrated in figure 4 of Ref. [14].

In a previous study, we showed the consistency of our results in terms of the size slab [12]. In the present work, we report the projected bulk bands in the valence band region, and we discuss the surface and resonance states found at these energies.

This paper is organized as follows: Section 2 briefly describes the method used in our calculations. In Section 3, we discuss our results. Finally, our conclusions are presented in Section 4.
2. Methods

The method used in our calculations was the full-potential linearized augmented plane-wave method (FP–LAPW), as implemented in the WIEN2k code [16]. The exchange–correlation energy was calculated using the GGA correction of Perdew et al., [17]. In our calculations, the employed atomic electronic configuration was Zn: [Ar] 4s 3d; Se: [Ar] 4s 3d 4p; Cd: [Kr] 5s 4d; and Te: [Kr] 5s 4d 5p, in which the Zn–3p and Cd–4p states were treated as valence-band states using the local orbital extension of the LAPW method [16]. During the calculations, a step analysis was carefully performed to ensure the convergence of the total energy in terms of the variational parameters; here, we selected the following values: 9 for $R_{MT}K_{max}$ (where $R_{MT}$ is the muffin-tin radius and $K_{max}$ is the plane-wave cutoff) and 15 Ry for the cutoff energy parameter ($G_{max}$) for CdTe(001) were used, whereas values of 8.5 for $R_{MT}K_{max}$ and 12.0 Ry for $G_{max}$ were used for CdSe(001); for ZnSe(001), the values used were 8 for $R_{MT}K_{max}$ and 15 Ry for $G_{max}$. Additionally, an appropriate set of k–points in the irreducible sector of the Brillouin zone was used; here, a value of 28 k–points for all cases were taken into account. Finally, we relaxed all of the atoms in the slab using Hellmann–Feynman forces until the force component was less than 0.5 mRy/au.

From the slab construction, we can distinguish different atomic sites for the cations (Cd, Zn) and for the anions (Te, Se). Thus we can identify the cation–1, which is located on the surface, and cation–3 and cation–5, which are located on the third and fifth atomic layers, respectively. Then, for the nearest-neighbor layer to the surface, we identify the anion–2 atoms, and the anion–4 and anion–6 atoms are located on the fourth and sixth atomic layers, respectively. This identification of the different atoms will be useful in the discussion of our results (see Fig. 4 in Ref. [14]).

3. Results

3.1. Geometry optimization

From the structural optimization procedure, we observed that all of the inner atomic layers are fixed, except for the two outermost atomic layers. That is, we found that the surface cation1 layer moves downward while the second layer, the anion2–atoms, moves upward in such a way that both atomic planes are located quite near each other. In fact, the relaxed anion2–cation1–anion2 angle is significantly different from the bulk value (see Table 1). Thus, the relaxed nearest-neighbor distances are quite different from their corresponding bulk values. The new nearest-neighbor bond lengths are shorter than their corresponding bulk values. As the anion2–layer moves upward, the bond length between the second atomic layer and the third atomic layer increases. Previous studies have shown that during the relaxation of the II–VI (001) $C(2 \times 2)$ surface, the cation layer relaxes downward while the anion layer relaxes upward; [1, 11, 13, 14, 15] our obtained results are in agreement with these previous studies.

Table 1 presents our calculated bond length values for the different systems studied in this work, and for comparison, we also include the values measured or calculated in other works. As shown, our calculated values for the different bond lengths are in good agreement with the measured and calculated values reported in the literature. However, note that the calculated LDA lattice parameters are generally smaller that the GGA ones, as is shown for the case of CdSe(001) [13].

3.2. Partial density of states

We have verified that our slab model appropriately reproduces the known bulk electronic density of states of the investigated systems. To prove this ability of our model, we compared the calculated partial density of states (PDOS) of the inner atoms of the slab with the bulk PDOS. Figure 1 shows the calculated PDOS for the different systems investigated in this work. As shown in this figure, the calculated PDOS for the upper valence band (VB) for the atoms located
Table 1. Calculated and reported values for the nearest-neighbor (nn) bond length, the bond length between the second and third atomic layers (nnn), the anion–anion (A2–A2) interlayer distance, and the anion2–cation1–anion2 angle for the different systems studied. The figures in brackets are the bulk values, and all of the bond lengths are reported in Angstroms (Å).

| System       | Present work | Other works |
|--------------|--------------|-------------|
|              | nn           | nnn         | A2–A2 angle | nn           | nnn         | A2–A2 angle |
| CdTe(001)    | 2.66 (2.81)  | 3.03        | 3.89 (4.58) | 167.06°      | 2.62        | 2.81        |
|              |              |             |             |              | 2.63        | 3.92        |
| CdSe(001)    | 2.55 (2.62)  | 2.80        | 3.58 (4.28) | 154.33°      | 2.44        |
| ZnSe(001)    | 2.33 (2.45)  | 2.57        | 3.52 (4.01) | 149.40°      | 2.23        |

aMeasured [1]; bCalculated [11]; cCalculated [13]; dMeasured [14]

Figure 1. (Color online) Calculated PDOS for the different systems investigated in this work. The calculated bulk PDOS is shown as a solid line, the PDOS for the central layer atoms of the slab is shown as a blue line, and the PDOS for the atoms located on the surface is shown as a red line. The upper panel shows the cation PDOS, and the lower panel shows the anion PDOS.

in the central layer of the slab is almost similar to that obtained from the bulk calculations. The same agreement is observed for the PDOS of the lower conduction band (CB). In the case of CdTe, the energy difference for the main peaks in the VB is less than 0.11 eV in both the Cd– and Te–atomic layers.

However, we observed that differences are observed mainly for the atoms located in the outermost surface layers. These differences are associated with the existence of surface and resonance states, as discussed below.

In all of the cases shown in the figure, we observe that the surface cation PDOS exhibits important features at approximately 3.5 eV below the Fermi level and in the lower part of the CB. Furthermore, important features due to the anion second atomic layer are also obtained. In the VB energy region shown, the anion PDOS spreads more than the cation case.

3.3. Surface– and Resonance– states
The electronic states at the surface of a single crystal are strictly two–dimensional and show a dispersion that differs significantly from the bulk states. It is convention to distinguish between surface states (empty surface states), which lie in the projected band–gap, and surface resonances (occupied surface states) [21], which lie within the bulk band structure projected on the surface. These states originate once we break the translational symmetry to create the surface.

We have shown in Fig. 1 that our results for the CdTe(001) and ZnSe(001) surfaces are quite similar to those for the CdSe(001) case; thus, and to save space, we will only discuss the CdSe(001) C(2 × 2) case in detail; further details for the other surfaces will be provided elsewhere [23].

Figure 2 shows the calculated electronic bands in the first Brillouin zone of the
Figure 2. (Color online) Projected surface bulk bands for CdSe(001) C(2 × 2). The bands are shown in the irreducible Brillouin zone of the unreconstructed (1 × 1) surface.

unreconstructed (1 × 1) surface, in which the contributions of the surface-layer atoms to the surface states are indicated with circles. A larger circle size corresponds to more charge within the atomic sphere of the respective layer [16], and thus indicates an important contribution to the electronic bands of the atoms on the surface layers compared with the atoms located in the inner layers.

As indicated in Fig. 1, we obtained a number of surface and resonance states associated with the atoms located in the two outer layers of the slab.

In Fig. 2, we identify a series of resonance states associated with both the external Cd1 atoms (left panel) and the nearest-neighbor Se2 atoms (right panel).

For Cd1, we obtained a resonance state located at approximately 3.0 eV below the VB maximum. The state shows a wavy dispersion shape. Then, in the range from approximately 0.8 to 2.0 eV above the VB maximum, we obtain a surface state. The surface state follows the dispersion of the minimum of the CB. We observed that the obtained surface and resonance states have the symmetry of the Cd s− and p−orbitals hybridized with the Se p−orbitals [23].

The right panel of the figure shows that in the upper VB energies, there are two surface states associated with the Se2 atom. At the upper VB, we obtained a surface state that follows the dispersion of the VB maximum; this state mainly has Se p−character. Then, we obtained a resonance state at approximately −0.1 eV. The state has anion p−x−character. Both states span over the shown Brillouin zone.

We also found that the Se2 atom contributes to the mentioned cation surface states, as noted in Fig. 1.

At the upper CB energies, there are some traces of resonance states; however, we will omit further discussion of these states.

Although we have identified that the cation lower CB and the anion upper VB states are surface states [24], previous works have claimed that for the II–VI C(2 × 2) surfaces, there are only resonance states in the VB [11, 15].

4. Conclusions

We investigated CdTe(001) −, CdSe(001) −, and ZnSe(001) − C(2 × 2) reconstructed surfaces using first-principles calculations. We found that our slab model reproduces the experimentally measured structural bond lengths, and the bulk partial density of states was also well reproduced in our model. The surface and resonance states reported from experimental results and in previous calculations were also found in our calculations.

Although recent ab initio calculations do not support the existence of surface states on the studied surfaces, we found a band gap surface state that shows an important dispersion as a
function of $k$, which was also observed in previous empirical calculations. We will report a detailed investigation on the different features found in this work in a future study.

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In a future work we will present a full discussion of the different features found for other II–VI semiconductors.

Using the empirical tight–binding approach and the surface Green function matching method, the lower CB surface state was found in previous work for the CdTe(001), ZnTe(001), and HgTe(001) ideal surfaces. [10] There it was found that the surface state does not show dispersion and was located almost in the mid band gap of the studied compounds. Also, it was argued that for a relaxed and reconstructed surface, the surface state should present some dispersion.