Electronic band structure of the CdTe $C(2 \times 2)$ reconstructed surface: 
\textit{ab initio} study in terms of the slab size

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The structural and electronic properties of the $C(2 \times 2)$ reconstructed CdTe(001) surface have been studied in the framework of the first principles calculations. In this work we have used the slab model, and we analyze our results in terms of the slab size. We compare our results for a slab of nine monoatomic layers vs. a seventeen monoatomic layers slab. In both cases, we use four atomic layers of vacuum. Using the experimentally determined lattice parameter as input we have optimized the internal structural parameters (atom positions) of the outer atomic layers. We show that our model reproduces well known electronic properties found in bulk CdTe. Finally, we present our calculated projected bulk band structure and we discuss the surface and resonance states.

Keywords: Ab initio calculations; II–VI compounds; surfaces.

Utilizando métodos de cálculo de primeros principios estudiamos las propiedades estructurales y electrónicas de la superficie (001) del CdTe con reconstrucción $C(2 \times 2)$. En nuestro estudio utilizamos el modelo de capas y analizamos nuestros resultados en términos del número de capas usado. Los modelos estudiados incluyen un conjunto de nueve capas mono–atómicas y otro de diez y siete capas mono–atómicas, en ambos casos incluimos cuatro capas de vacío. Utilizando el parámetro de red experimental, optimizamos las posiciones atómicas de los atóm conanas externas. Encontramos que nuestro modelo reproduce propiedades electrónicas conocidas en el volumen infinito del CdTe, y como resultado de nuestro estudio mostramos la estructura electrónica de bandas proyectada en el volumen y discutimos los estados de superficie y estados resonantes hallados.

Descriptors: Cálculos \textit{ab initio}; compuestos II–VI; superficies.

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\section{1. Introduction}

II–VI semiconductors have received ever increasing attention in view of their application to optoelectronic devices for the detection and stimulated emission in the IR (mainly CdHgTe), as well as in the 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 CdTe(001) surface shows different reconstructions, as a function of temperature. The knowledge of the atomic structure of these surfaces is crucial for understanding the energy band structure, and consequently, for the tailoring of heterostructures with given electronic properties. The CdTe(001) surface has been studied experimentally in early work \cite{1,2,3}, as well as theoretically in an empirical approach \cite{4,5} and by using first principles calculations \cite{6}.

In this paper we report the study of the CdTe(001) $C(2 \times 2)$ reconstructed surface. To study the (001)–surface we have used the slab model. We present a comparative study using two different slabs. We have constructed one slab of nine monoatomic layers and four atomic layers of vacuum. The slab is formed by multiples of the lattice vectors $a$, $b$, and $c$, like the $1 \times 1 \times 2$ slab, where in the $a$ and $b$ directions the slab has one unit cell, while in the $c$ direction the slab has one unit cell of vacuum, then two unit cells of CdTe in the Cd–Te–…–Te–Cd monoatomic layer sequence, and finally one unit cell of vacuum. For future reference we will call this model the 112–slab. Then a second slab with four unit cells of CdTe in the $c$ direction, as well as one unit cell of vacuum at the ends of the slab, was studied. This slab contains seventeen monoatomic layers in the same monoatomic order as the 112–slab, and will be called the 114–slab. The $C(2 \times 2)$ reconstructed surface is schematically shown in Fig. 1.

The paper is organized as follows: Sec. 2 briefly describes the method used in our calculation; in order to save space, we will refer to the appropriate references for a full discussion of the method. In Sec. 3, we discuss our results. Finally, Sec. 4 contains our conclusions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{Structural model for the CdTe(001) $C(2 \times 2)$ surface. (a) top view, (b) side view. The reduced $c(2 \times 2)$ unit cell is shown as a gray area. Small arrows indicate the direction of the relaxation of the atoms. Grey symbols represent Cd atom, bold symbols are for Te.}
\end{figure}
2. Method

In our calculations we have used the full potential linearized augmented plane wave method (FP–LAPW) as it is implemented in the Wien2k code [7], and we use the GGA correction for the exchange–correlation part of the total energy [8].

In order to find the minimum of the total energy in each slab as a function of the k–points in the irreducible sector of the Brillouin zone and as a function of the cutoff energy, we have used a set of 16 k–points and a value of 17 Ry for the cutoff energy in the 112–slab, while for the 114–slab, a set of 28 k–points and the value of 15 Ry for the cutoff energy were used. Then we have relaxed the atomic positions in the outer layers using the Hellmann–Feynman forces until the force component was below 0.01 eV/Å.

In the 112–slab model we can distinguish three different kinds of Cd–atoms. The Cd1 atoms located on the surface (atomic layer 1 in Fig. 1), the Cd3 atoms located on the XZ and YZ planes (layer 3), which by symmetry all of them are identical, and the Cd5 atoms located on the central layer (layer 5). At the same time we can distinguish two different kinds of Te–atoms. The Te2 atoms located on the nearest neighboring plane to the surface (layer 2), and the Te4 atoms located on the fourth plane.

Then, in the 114–slab we can distinguish five atomic positions for Cd and four atomic positions for Te. We have the Cd1 atoms located on the surface, the Cd3 and Cd7 atoms located on the third and seventh atomic layers, respectively, the Cd5 atom located on the fifth atomic layer, and the Cd9 atom located on the central layer. Finally, in the nearest neighboring layer to the surface, we have the Te2 atoms, the Te4 and Te6 atoms located on the fourth and sixth atomic layers, and the Te8 atom located on the eighth atomic layer.

3. Results and Discussion

We have allowed to relax the outer layer (the Cd–plane) and the second atomic layer (the Te–plane) in such a way that the top Cd1 atoms move downward until they are almost in the same Te atom plane, and the relaxed nearest neighboring distances are different from the bulk bond distances. The new Cd–Te bond lengths are 2.66 Å for the 112–slab and 2.75 Å for the 114–slab. While the Te–plane moves up, it increases its bond length with the third layer (Cd–plane) to 2.91 Å in the 112–slab and to 3.03 Å for the 114–slab. In comparison with the bulk bond length (namely 2.81 Å) we obtain that the two outer planes become closer than in the ideal surface, while the second and third planes increase their bond distance.

According to Gundel et al. [6] the Cd–Te bond length at the surface is about 6.1% shorter than in CdTe bulk. In our calculations we found that the Cd–Te bond length at the surface is 5.5% shorter than the bulk bond length for the 112–slab model, and 2.0% shorter than the bulk value for the 114–slab model. Although our values are slightly different from the previously reported values [3, 6], they show the correct trend.

Figure 2 compares the calculated LDOS for bulk CdTe (bold line) with the calculated LDOS for the atoms located on the surface (broken line) and the atoms located on the central layers (full line) for the 112–slab. As we can observe, the calculated LDOS for the atoms in the central layers are similar to the LDOS obtained for bulk CdTe. The energy difference for the main peak in the valence band (VB) is less than 0.2 eV in both cases. The main difference is observed for the atoms located in the outer surface layers. These differences are associated with the presence of surface and resonance states [6].

As it is well known, the LDOS for Cd mainly have the Cd 5s−character, with few contributions from the Cd 4p−orbitals. The LDOS for Te mainly have the Te 5px−and 5py−character, with small contributions from the Te 5s−orbitals.
Figure 3 compares the calculated LDOS for bulk CdTe (bold line) with the calculated LDOS for the atoms located on the surface (broken line) and the atoms located on the central layers (full line) for the 114–slab. In this case we found that the energy difference for the peaks in the VB region is 0.11 eV. It is observed that the intensity of the peaks associated with the surface and resonance states is more defined in this case than in the previous one.

Figures 4 and 5 show the contribution of the atoms on the surface for the slab models studied in this work to the projected bulk bands (PBBs).
We show the PBBs in the first Brillouin zone of the unreconstructed (1 × 1) surface.

In the figures we show the contribution of the surface atoms by circles. A bigger size of the circle means an important contribution to the PBBs of the surface atoms in comparison with the atoms of the inner layers.

As was commented in Figs. 4 and 5, we obtain a set of surface and resonance states associated with the atoms located in the two outer layers of the slab.

In Figs. 4 and 5 we identify two resonance states associated with the Cd1 atom in the studied slabs. These states show big dispersion and are located around 3. eV in the CB and at −3.0 eV in the VB.

Also we obtain a surface state following the dispersion of the minimum of the CB. This state is obtained at 1. eV.

We found that the obtained surface and resonance states have the symmetry of the Cd 5s-orbitals.

These results are consistent with the calculated LDOS shown in Figs. 4a and 5a.

The figures also show an important set of resonance states associated with the Te2 atom, the atom located in the second monoatomic layer from the surface. These facts are coherent, since we know that the main contribution to the bands in this interval of energy of the VB is obtained from the Te 5p–orbitals, as we have commented in Figs. 4 and 5.

We can observe that the resonance states commented for the Cd1 case also have an important contribution in the Te2 orbitals. This is due to the strong hybridization of the Te 5p– and Cd 5s–orbitals in the VB.

Then, we observe a surface state following the dispersion of the VB maximum from \( K - \Gamma \); this state has the Te 5p\( z \)–character.

Also, we obtain a resonance state around −1. eV with the Te 5p\( z \)–character. In the rest of the VB we obtain important hybridization of the Te 5p\( z \) and 5p\( y \)–orbitals.

The resonance states in the CB have the Te 5p\( y \) and 5p\( x \)–character, while the surface state following the dispersion of the CB minimum mainly has the Te 5p\( y \)–character.

These resonance and surface states were also found in a recent \( ab \) initio pseudopotential study by Gundel et al. [6]. The states have also been reported in previous work using an empirical tight–binding approach and surface Green formalism for CdTe(001) and other II–VI compounds [4, 5]. The resonance and surface states have also been studied in ZnSe(001) \( C(2 \times 2) \) reconstructed surfaces, both experimentally and theoretically [9, 10].

In a future work we will report a detailed analysis of the differences and other features found in the slab models presented in this study [11].

4. Conclusions

We have studied the CdTe(001) \( C(2 \times 2) \) reconstructed surface using first principles calculations. We have found that using a minimal slab model reproduces the surface and resonance states reported in experimental reports as well as in previous calculations. In a future work we will report a refined study of the different features found in our calculations.