# Electronic band structure of (001)–semiconductor surfaces: the frontier–induced semi–infinite–medium states.

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In previous work we have discussed the valence band electronic structure of the (001) oriented semi–infinite medium of the II–VI wide band gap zinc–blende semiconductor compounds. We have found three characteristic surface resonances besides the known bulk bands (heavy hole, light hole and spin–orbit bands). Two of these resonances correspond to the anion–terminated surface and the third one to the cation terminated surface. Furthermore, we have shown that three non dispersive (001)–surface–induced bulk states, in the $\Gamma - K$ direction of the 2D Brillouin zone, are also characteristic of these systems. To identify these states, from other known surface states, we have called them frontier–induced semi–infinite–medium states. In order to continue with the description of these systems, we review the main characteristics of the electronic structure of the (001)–surfaces and we present a detailed theoretical discussion of the frontier–induced semi–infinite–medium states. We use tight binding Hamiltonians and the well–known Surface Green's Function Matching method to calculate the electronic surface band structure.

*Keywords:* Electronic states; surface resonances; tight–binding method

En un trabajo previo hemos calculado la estructura electrónica de bandas de las superficies orientadas en la dirección (001) de compuestos semiconductores de la familia II–VI. De ese trabajo hemos hallado que, además de las bandas de volumen conocidas (bandas de huecos pesados, huecos ligeros y espín–órbita), existen en estos sistemas tres resonancias de superficie. Dos de estas resonancias están asociadas con una superficie terminada en anión, y la tercera resonancia se asocia con la terminación catión de la superficie. También, hemos hallado que existen tres estados electrónicos localizados en valores de energía que no presentan dispersión como función del vector de onda en estos sistemas bidimensionales. Para identificar estos estados hemos propuesto el nombre de estados de frontera inducidos por un medio semi–infinito. Con el interés de continuar el estudio de estos sistemas, en el presente trabajo hacemos una revisión del estado del arte de la estructura electrónica de bandas de las superficies semiconductoras orientadas en la dirección (001), y presentamos un estudio teórico detallado de los estados frontera inducidos por un medio semi–infinito. Para nuestro análisis utilizamos el método de enlace fuerte y el método empalme de la función de Green de superficie en el cálculo la estructura electrónica de bandas de la superficie.

*Descriptores:* Estados electrónicos; resonancias de superficie; método de enlace fuerte

## 1. Introduction

The electronic band structure of the valence–band of the II–VI wide band gap semiconductors CdTe, ZnTe, CdSe and ZnSe semi–infinite crystals terminated in the (001)–surface has been discussed in Refs. 1 and 2. The calculated electronic band structure of the valence band of the (001)–surface is very rich in several features. In general, we find three characteristic surface–resonances in the energy range studied (full and empty triangles in Fig. 1. Two correspond to the anion–terminated surface ($S_{a1}$, $S_{a2}$) and the third one to the cation terminated surface ($S_c$). The anion–terminated surface–resonance ($S_{a1}$) follows roughly the dispersion of the heavy hole bulk band, but at a slightly higher energy (see Fig. 1. The $S_{a2}$ surface resonance does not show dispersion and, approximately, coincidences with the lower bulk band of $s-$character. The cation terminated surface–resonance ($S_c$) starts roughly around 2–3 eV from the top of the valence band in $\Gamma$ and has a varying amount of dispersion, depending on the compound. These surface resonances are characteristic of the kind of atomic species on the surface (see Refs. 1 and 2).

On the other hand, by looking at the poles of the real part

of the (001)–bulk–projected Green's function we obtain the eigenvalues of the (001)–surface–induced bulk states. Three such states appear ($B_h$, $B_l$, and $B_s$) in this range of energy. These surface–induced bulk bands do not show dispersion from $\Gamma$ to $K$. We find that the energy of these states can be associated with the one of the hh, the lh, and *so* bulk band at $K$, the 2D–high–symmetry point [1, 2]. Thus, at $K$, $B_h$ mixes mainly with the hh bulk band and $B_l$ with the lh one, both states are mainly of $(p_x, p_y)$–character. $B_s$ mixes with the spin–orbit band and is mainly of $(s, p_z)$–composition (see Table IV in Ref. 2). The three states appear at the same position in energy irrespective of the cation or anion termination of the surface, as can be expected for a surface–induced *bulk* states, since they must depend on the surface only through the boundary conditions (the wave function must be zero at the surface). Furthermore, we have found these induced bulk states at the (001)–interfaces as well. In order to extend this study to the case of interfaces, and other type of heterojunctions as well, and to emphasise the idea that they are semi–infinite medium states as opposed to bulk (infinite medium) or surface (local) states, we propose for them the generic denomination of Frontier–Induced Semi–Infinite
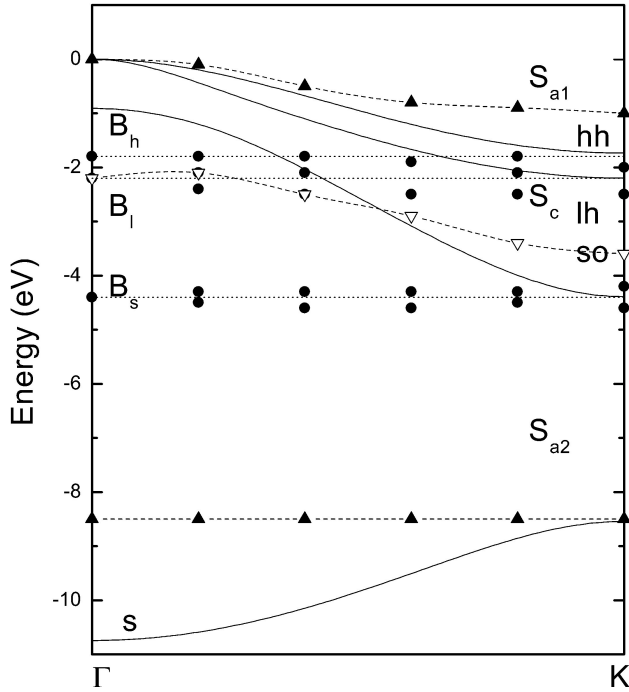
FIGURE 1. Electronic band structure of (001)–CdTe in the valence band range. We show the heavy hole (hh), light hole (lh), spin–orbit (so), and the lower $s$–cation character bulk bands with solid lines. We also show the FISIM states $B_h$, $B_l$, and $B_s$ (solid points), and the surface resonances $S_{a1}$, $S_{a2}$ (solid triangles), and $S_c$ (open triangles), the broken lines are a guide to the eye. The first two surface resonances appear only for an anion–terminated surface, and the last resonance for a cation–one.

Medium (FISIM) states. We found experimental evidence for the FISIM states on the (001)-CdeTe oriented semi–infinite crystals [3, 4], and on the (001)–ZnSe system [5–7], and we feel that a full theoretical interpretation of the electronic band structure for these semi–infinite systems is missing. With this purpose, in this work, we present a detailed theoretical discussion of the FISIM states. The rest of the paper is organized as follows. In Sec. 2, we describe the method that we have used. Sec. 3 is devoted to the discussion of the FISIM states. We summarize our conclusions in a final Sec. 4.

## 2. The method

The Schrödinger equation, with the appropriate Hamiltonian describing an infinite periodic system, gives the Bloch wave functions and the energy eigenvalues. The Bloch wave functions fulfil periodic boundary conditions. When a surface is introduced, and the system becomes semi–infinite, the boundary conditions are such that the wave function has to be zero at the surface. These new boundary conditions manifest themselves in changes in the energy spectrum and in the occurrence of new states. These new states exist only in the few atomic layers nearby the surface atomic layer. Their

wave function decays exponentially from the surface into the bulk. On the other hand, there are other states that do not decay exponentially from the surface, and can exist in layers inside the semi–infinite medium, but have a 2D character and therefore can only be detected by photoemission of an oriented crystal. All these effects related with the introduction of a surface into an infinite periodic medium can be better described in the language of Green's functions. A few words about the bulk Green function will help us to introduce the surface Green function. As it is well know, the infinite periodic medium Green's function, $G$, is

$$G(E, \mathbf{k}) = (E - H(\mathbf{k}))^{-1}, \qquad (1)$$

where $\mathbf{k}$ is the crystal momentum, $E$ is the quasiparticle energy and $H$ the Hamiltonian for the infinite periodic system with translational symmetry, periodic boundary conditions are assumed. However, as soon as we are interested in the semi–infinite medium, we have to introduce the Green's function for a semi–infinite medium [8]:

$$G_s = G - G\mathcal{G}_B^{-1}G + G\mathcal{G}_B^{-1}\mathcal{G}_S^{-1}\mathcal{G}_B^{-1}G, \qquad (2)$$

where the first term in the right hand side is just the Green's function for the infinite medium. The second and third terms describe the total effect of introducing a surface to an infinite medium. The second term describes the hard wall effect, in close analogy to the hard core term in scattering theory. The third term describes the new states, the new solutions due to the matching conditions and give rise to surface states that decay few atomic layers away from the surface.

In order to compute the bulk (infinite medium) band structure of the II–VI semiconductor compounds we have used the empirical tight–binding (TB) method in the Slater–Koster formalism [9, 10]. We have used an orthogonal basis set of five atomic orbitals per atom in the unit cell, ($s\ p^3\ s^*$), and we have included the effect of the spin–orbit interaction [11]. As is widely accepted, this representation gives an acceptable description of the electronic band structure of the semiconductor compounds [10, 12, 13].

To study the (001) surfaces we use the Surface Green's Function Matching Method (SGFM) in the appropriate tight–binding representation [8, 14, 15]. This method uses as input the bulk tight–binding parameters (TBP). The difference between the bulk TBP and the surface ones is taken into account through the matching in the SGFM method [8]. We have calculated the (001)–bulk–projected ($\mathcal{G}_B$) and the (001)–surface–projected ($\mathcal{G}_S$) Green's functions, given in Eq.(2). From $\mathcal{G}_B$ we can obtain the changes in the electronic band structure derived from the hard wall effect (second term contribution in Eq. 2) and from $\mathcal{G}_S$ we obtain the surface band structure (third term contribution). To calculate these Green functions we use the known formulae [14, 15]

$$\mathcal{G}_S^{-1} = (E - H_{00}) - H_{01}T, \qquad (3)$$

$$\mathcal{G}_B^{-1} = \mathcal{G}_S^{-1} - H_{10}\widetilde{T}. \qquad (4)$$

The way in which the Hamiltonian matrices are relate to the TB Hamiltonians is described in detail in references [14, 15], we will omit further details here. $T$ and $\widetilde{T}$ are transfer matrices depending only on $H_{00}$, $H_{01}$ and $H_{10}$, the principal–layer–projected Hamiltonian matrices [16]. Quickly converging algorithms to calculate the transfer matrices were first obtained by López Sancho *et al.* [17]

## 3. The FISIM–states

### 3.1. The experimental evidence

#### *3.1.1. (001)–CdTe*

One of most capable techniques to determine absolute critical point energies and energy dispersion curves is the angle resolved photoelectron spectroscopy (ARPES). From the ARPES data for CdTe(001), obtained by Niles and Höchst [3], the measured spin–orbit splitting $\Delta E_{SO} = 0.95$ eV agrees well with earlier electroreflectance and photoluminescence measurements [18, 19]. The experimentally determined dispersion of the heavy– and light–hole valence bands agrees well with predictions based on nonlocal pseudopotential calculations [20]. For the width and dispersion of the split–off valence band, however, Niles and Höchst found a small but noticeable discrepancy with theoretical predictions [20, 21]. Their data imply a width of 4.4 eV, whereas nonlocal pseudopotential calculations predict 5.05 eV. Furthermore, in their ARPES report, Niles and Höchst notice the persistence of photon momentum independent emission at 4.4 eV. In Fig. 6 of Ref. 3, they report a non–dispersive ($k$−independent) band measured up to about half the way from $\Gamma - X$. They attribute this state to indirect transitions from a high–density–of–states region around the critical valence band point $X_6$.

Later on, Gawlik *et al.* [4] investigated an unreconstructed CdTe(001) surface prepared by ion bombardment and annealed using angle resolved photoemission. To separate surface and bulk related spectral features they used different criteria. They found, at 4.6 eV binding energy, a weakly dispersing band which contains, according to them, mixed surface and bulk character. The high density of bulk states associated with this edge of the heteropolar gap, they add further, is also expected to contribute to this feature.

#### *3.1.2. (001)–ZnSe*

In later work, Lopinski *et al.* [5], Zhang *et al.* [6], and Chen *et al.* [7] have reported experimental results on the (001)–ZnSe system. From these new results, we find further support to our calculated anion–type resonances and FISIM states. Also, the upper anion valence band surface resonance has been predicted in *ab initio* calculations, by Park and Chadi [22], and is in agreement with the experimental measurements. Our calculated dispersion for this surface resonance is found to be in correct correspondence with both results,

the theoretical and experimental ones (see Table I of Ref. 6). On the other hand, Zhang *et al.* discuss the possibility that some of their measured structures could be related with our lower anion–type surface resonance and with our $B_l$ and $B_s$ FISIM states. Alternatively, they identify the last two states as bulk umklapp transitions.

More recently, Chen *et al.* [7], in a photoemission study of the Na/ZnSe(001) system, have identified their measured band structure with our predicted FISIM states ($B_h$, $B_l$, $B_s$). Their measured peak are for a ZnSe (100)c(2 × 2) surface (cation terminated surface). Their structures are at 0.6, 1.6, 2.7, and 5.0 eV from the top of the valence band. The last experimental peaks can be directly related to our $B_h$, $B_l$, and $B_s$ states, calculated at 2.0, 2.3 and 5.3 eV from de top of the valence band [2], respectively. Although, according to the experimental report, the measurements have been done with deficient angle resolved precision, we think that the experimental results support widely our predictions.

The rest of the work will be devoted to discuss our theoretical interpretation of the FISIM states. For this purpose we will use the already discussed experimental information for the (001)–CdTe surface. Although, similar arguments could be applied to the other cases.

### 3.2. Theoretical interpretation

We think that although at slightly different energies, the experimental results of Niles and Höchst and Gawlik *et al.*, report on the same non–dispersive state at ∼ 4.4 eV. Niles and Höchst attribute their signal to indirect transitions from a high–density–of–states region around the $X_6$ valence band critical point. Gawlik *et al.* assign this state to a mixed surface and bulk character, although they found plausible the explanation given by Niles and Höchst. We will look now at the indications given by our calculations in this sense. First, let us point out that we have calculated the bulk bands in agreement with experiment and the *ab initio* calculations. We have refined the TBP to reproduce more accurately the experimental results at the $X$−point of the Brillouin zone, as we have already remarked [1, 2].

We obtain the non–dispersive state as a solution of the 2D–projected bulk Green's function (as the poles of the Green function) at the energy of 4.4 eV for the whole $\Gamma - K$ interval. The state appears to have a slight dispersion. In contrast to this, when we look at the surface Green's function we do not see traces of this state. This point is dealt with in detail in Ref. 1. In this sense we conclude that the state is of semi–infinity medium character. This is our definition of surface induced bulk states.

To further clarify this point, we have calculated for the (001)–CdTe unreconstructed surface the 2D density of states, $N(\omega)$, for the (001)–CdTe unreconstructed surface, projected onto the first 11 atomic layers from the surface into the bulk. $N(\omega)$ is proportional to $\mid \Psi \mid^2$, where $\Psi$ is the semi–infinite medium wave function for this state with energy eigenvalue
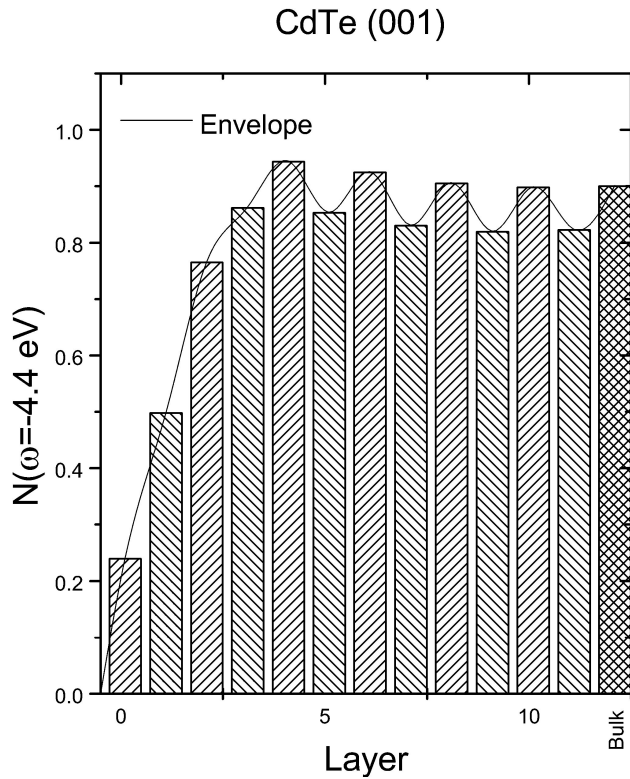
## CdTe (001)



FIGURE 2. 2D density of states $N(\omega)$, for the unreconstructed CdTe (001)–surface projected onto the first 11 atomic layers. $N(\omega)$ is calculated at the energy eigenvalue –4.4 eV, corresponding to the $B_s$ state in Fig. 1, and integrated over the 2D Brillouin zone. $N(\omega)$ does decay towards the surface but into the bulk it takes a constant value, showing that the $B_s$ state is of semi–infinite character.

–4.4 eV. The projected density of states is obtained by integrating in the 2D first Brillouin zone using the method of Cunningham [23]. Here we have used a set of 16 special points in the 2D–BZ. For numerical convergence a small imaginary part of 0.001 eV to the real energy variable was added. Our result is showed in Fig. 2. From the figure it is clear that $N(\omega = -4.4 \text{ eV})$ does decay towards the surface but from the 5th atomic layer on from the surface into the bulk it takes a constant value, different for a cation and for an anion atomic plane, but constant as one expects for a bulk state. We do not find any surface character attributable to this state. We stress that there is no exponential decay of the amplitude as one enters the bulk as it expected for a surface state. This state is actually neither of bulk (Bloch) character nor of surface character, strictly speaking. It is what we call a FISIM state.

A question remains to be addressed. Where these states come from? To answer this question, we have checked that the conservation law for the number of states within a band at constant **k** does hold. That is to say, if we integrate the 2D density of states over all the energy range at constant **k**, we obtain the same number of states per unit lattice in the bulk (Bloch–states) as for a system with a surface. In other words, any spectral weight for any new state, that appears due to a

change in the boundary condition, is removed from another one with the same **k**. If this is true,

$$\int [N_{\text{bulk}}(\omega, \mathbf{k}) - N_{\text{surface}}(\omega, \mathbf{k})]d\omega = 0.$$

$N_{\text{bulk}}$ being the bulk density of states for an infinite medium, and $N_{\text{surface}}$ the bulk density of states for a semi–infinite system projected onto the (001)–surface. We have checked that the integral over the energy is zero. Figure 3 shows this difference of the density of states for different **k**–values. This result shows indeed that the creation of a surface removes spectral weight from one energy–state to another at the same **k**. Thus, the new state is an LCAO combination of eigenfunctions of different energy but same quantum number **k**. This conservation law is a manifestation of the so–called Levinson's theorem [8, 24]. Our calculation therefore is not consistent with a spectral weight displacement from $X_6$ to other values of **k**, which would violate Levinson's theorem.
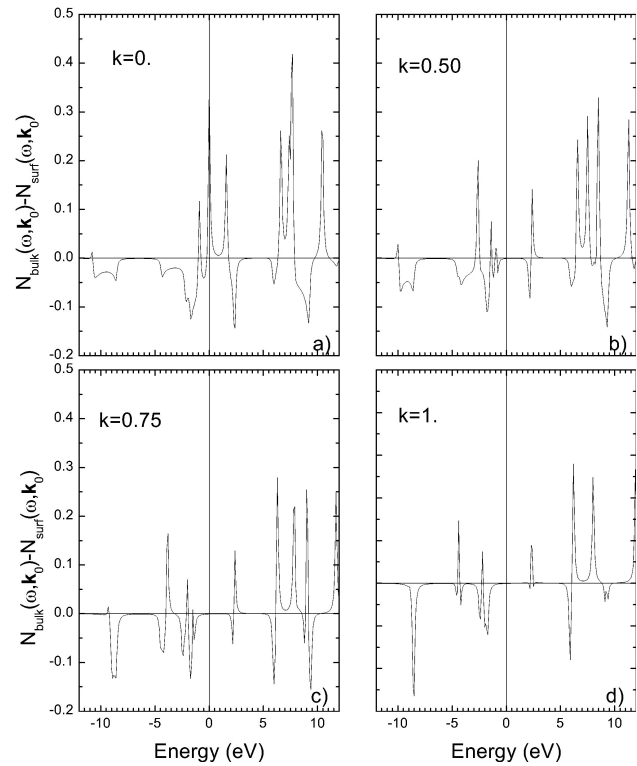


FIGURE 3. The difference of the density of states, $N_{\text{bulk}}(\omega, \mathbf{k}_0) - N_{\text{surface}}(\omega, \mathbf{k}_0)$ , for a fixed **k**–value. $N_{\text{bulk}}$ is the bulk density of states for an infinite medium, and $N_{\text{surf}}$ is the bulk density of states for a semi–infinite system projected onto the (001)–surface. This result shows that the existence of a surface shifts spectral weight from one energy state to another at the same **k**. The integral over the energy is zero, showing that the number of states with the same **k** is conserved. Here the calculation is for the $\Gamma$–point (a)), $\mathbf{k} = (2\pi/a)(0.5, 0)$ (b)), $\mathbf{k} = (2\pi/a)(0.75, 0)$ (c)), and for the $K-$ point (d)).

## 4. Conclusions

In conclusion, we have shown that in the II–VI direct band gap semiconductor compounds there are a new type of states that we have called the FISIM states. They are of semi–infinite medium character as opposed to surface character. We have shown that the density of states, projected onto the first ten atomic layers of the (001)–semi–infinite perfect crystal, for the energy eigenvalue of –4.4 eV, remains constant into the bulk and decays towards the surface. To better characterize the FISIM–states, we have calculated the difference between the bulk density of states for an infinite and a semi–infinite system. We have found that the FISIM–states, that appear in the semi–infinite system and do not appear in the infinite one, are LCAO built up from states of different energy but with the same **k**. They do follow Levinson's theorem. These are an added feature of the II–VI semiconductor valence band electronic structure and are of interest in applications as well as from the theoretical point of view.

## Acknowledgments

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