$CuInSe_2$: Electronic States for the Ideal Surfaces (100) and (112)

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Electronic states were calculated for the ideal surfaces (100) and (112) of the ternary compound $CuInSe_2$. The hamiltonians of the semi-crystals were obtained using the tight-binding method with s and p orbitals an basis for surface indium and selenium and s, p and d orbitals for copper. The Density of States (DOS) was calculated using Green's function and the transfer matrix method. The DOS shows energy states in the gap of the bulk material for both orientations.

I. Introduction

In recent years, the chalcopyryte $CuInSe_2$[1] has been studied because it is a promising material for technological applications e.g. in non-linear optics and in thin films based low cost solar cells. The calculation of the electronic structure of bulk, relevant technological surfaces and interfaces with other materials is important to the detailed understanding of the physics of devices.

The bulk electronic states of this material were studied by Jaffe and Zunger[2] using PVMB (potencial-variation mixed basis) assuming two independent zincblende sub-lattices. Their electronic bands are distributed in four sub-bands with three gaps in the valence band, and no sub-bands in the conduction band. In our preceding work[3], the main features of the bulk electronic structure of the $CuInSe_2$ were reproduced by a tight-binding method in agreement with the work of previous Jaffe and Zunger[2,1]; our Hamiltonian for the ideal bulk used a basis formed by s and p orbitals for indium and selenium and s, p and d for copper. The interaction was included up to first nearest neighbor using the Slater and Koster's model[5] with the Blom's adaptation to chalcopyrites[6] which we extended for d-orbitals[3]. For the non-diagonal elements of indium and selenium we used the Harrison's[7] rule which scales the tight-binding parameters with the inverse of the distance between atoms squared. Copper's tight-binding parameters were adjusted by the minimum square method to the optical gaps of the whole Cu-based chalcopyrites series[3].

In this work we show the Density Of States (DOS) at the ideal (100) and (112) surfaces and in the second, third and fourth atomic layers into the semi-infinite crystal; there are other no calculations of electronic states for (100) and (112) surfaces, to our best knowledge.

II. Model

Using our bulk tight-binding parameters[3], we calculate the Hamiltonians for two semi-infinity crystals: one finished in the ideal surface (100) and the other in the ideal surface (112); from them we calculate the DOS projected into the surface and the three next atomic layers. Using the surface Green's Function matching SGFM[8-10] method and the method of Cunningham integrate[11] in the first brillouin zone. The SGFM is useful because allows us to project the DOS on any inner layer and to follow its behavior from the surface layer into the crystal. We have considered that this semi-infinite crystal was built by stacking the principal layers which are made of two atomic layers. We considered only first nearest neighbor principal layer interaction. The surface Green's function can be written as[12]:

$$G_s(w, \mathbf{k}) = [w\mathbf{I} - \mathbf{H}_{00}(\mathbf{k}) - \mathbf{H}_{01}(\mathbf{k})\mathbf{T}(w)]^{-1} \qquad (1)$$

where w is the energy. We have used for the imaginary part of w 0.001; $\mathbf{k}$ is the two - dimensional wave number; $\mathbf{H}_{00}$ and $\mathbf{H}_{01}$, are the principal layer projections of the Hamiltonian. $\mathbf{I}$ is the unit matrix and $\mathbf{T}(w, \mathbf{k})$ the transfer matrix which can be calculated by the fast by converging algorithm of López-Sancho *et. al.*[7]. The DOS can be calculated from the imaginary part of $G_s(w, \mathbf{k})$.

III. Results

In figures 1 and 2 we show the DOS for the ideal surfaces (112) and (100) respectivelv. Additionaly, in these figures we also show the DOS for the second, third and fourth atomic layers; it is important to note that the surfaces and the third layer are made of cations (copper and indium), but the second and the fourth atomic layers are made of anions (selenium). The optical gap of the bulk is shown in each curve for reference.

In these figures we observe that the surface induced energy states appearing in the gap region of the bulk material. In the (112) surface these states are closer to the bottom of the conduction band (BCB) of the ideal bulk crystal and form a shallow sub-band; in contrast, in the (100) surface, we found deep states which are localized and sharper states. The DOS at the deep states of the (100) surface decreases quickly from the surface layer to inner layers; while the height of the states of the (112) surface decreases slowly. This behavior shows a significant difference between the surface which is due to the different enviroment for each atom in each surface.

In Figs. 1 and 2 we also observe localized resonances in the surface layer which disapear and the DOS progresively changes toward the characteristic electronic structure of the conduction band for the bulk material.

IV. Conclusions

A study of surfaces (100) and (112) of the $CuInSe_2$, using the tight-binding model has been presented. It is concluded that both surfaces show electronic states in the gap. In surface (112) those states give rise a sub-band while in the (100) surface they are localized and decay faster than the former.

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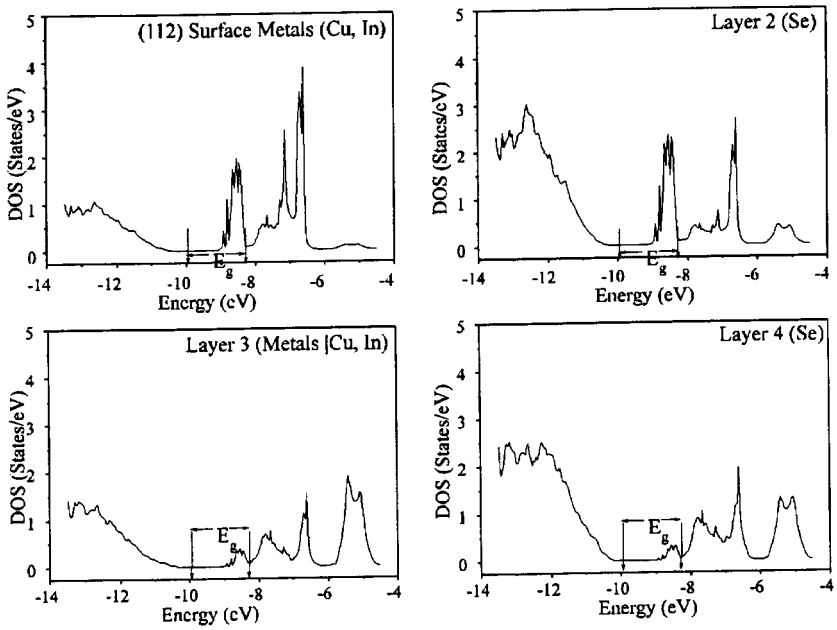

Figure 1. DOS for the (112) ideal surface of $CuInSe_2$.

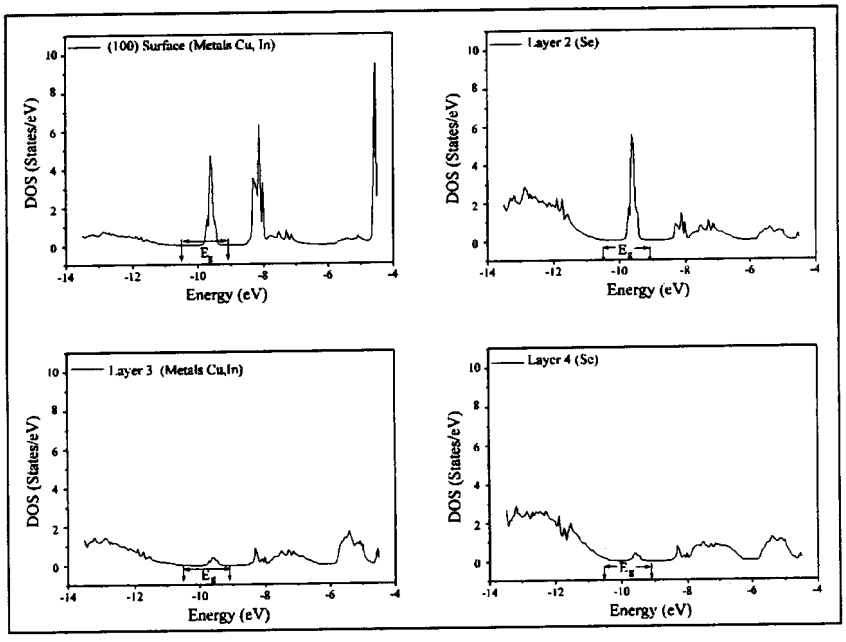

Figure 2. DOS for the (100) ideal surface of $CuInSe_2$.