PREDICTION OF THE BAND OFFSET AT THE ZnO/Cu_2O INTERFACE BASED ON THE FIRST-PRINCIPLE CALCULATION

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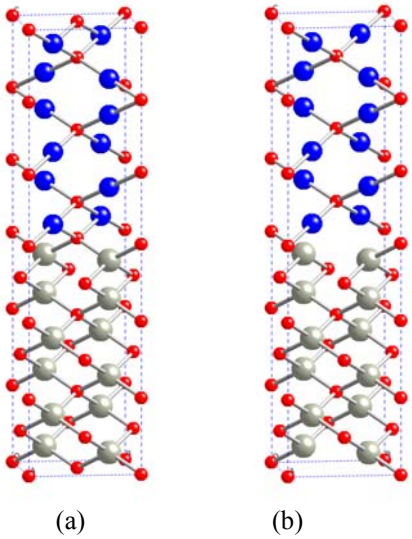
Introduction

Cu_2O is a p-type semiconductor with a band gap of 2.1 eV, and ZnO is an n-type semiconductor with a wider bandgap of 3.3 eV. The heterojunction of those two materials, Cu_2O/ZnO, is considered to be advantageous for solar cell application because 1) Cu_2O and ZnO have a suitable band gap for the absorber layer and for the window layer, respectively, 2) the constituent elements of those materials are all abundant, inexpensive, and non toxic. So far, the Cu_2O/ZnO heterojunction was fabricated by several methods, e.g., electrochemical deposition, sputtering, and oxidation of metals [1-4]. However, the reported efficiency is still low (1 - 2%). It is well known that the performance of a heterojunction solar cell is greatly influenced by the band alignment at the heterointerface. However, the band alignment of the Cu_2O/ZnO heterojunction has not been investigated in details either experimentally or theoretically. Thus, in this study, it is attempted to predict the band alignment at the Cu_2O/ZnO heterojunction on the basis of the first principle band structure calculation.

Calculation

The energy calculation was performed on the basis of the first principle, density-functional, pseudopotential method using the PHASE code developed by Inst. Industrial Science, Univ. Tokyo [5]. For the exchange-correlation energy, the generalized gradient approximation was used. To simulate ZnO/Cu_2O heterostructure, we consider the supercell shown in Fig. 1, where both ZnO and Cu_2O are assumed to have cubic crystal structure, and 6-monolayer-thick ZnO and Cu_2O layers are stacked alternately along (001) direction. We consider two type of the interface. In the first one (Fig.1(a)), oxygen atoms are arranged as in ZnO at the interface layer between ZnO and Cu_2O. In the second one (Fig.1(b)), oxygen atoms at the interface are arranged as in Cu_2O. Thus, in the latter case, the number of oxygen atoms at the interface layer is half of that in the former case. The lattice constant of Cu_2O is 0.427 nm, and that of ZnO is 0.454 nm. In the calculation, the average value (0.441 nm) was used for the lattice constant along the heterointerface. The lattice spacing in the perpendicular direction is assumed to be the same as in the respective bulk material. In this calculation, the ZnO and Cu_2O layers in the superstructure are considered to simulate the respective bulk material. Thus, the position of each atom was not optimized, i.e., the arrangement of the nearest neighbor atoms for each metal atom is the same as in the bulk material,



(a) (b)

Fig. 1 Supercells used for calculating ΔE_v, consisting of Cu_2O and zincblende ZnO. The small filled circles are O, the medium dark circles Cu, and the gray large circles Zn. The interface atomic layer is ZnO-like in (a) and Cu_2O-like in (b).

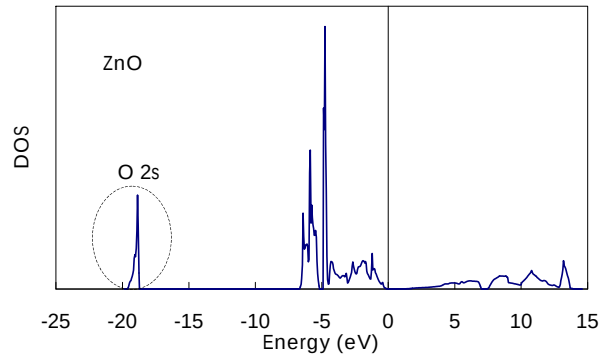
The band offset was calculated using a procedure analogous to the photoemission core-level spectroscopy [6]. The general formula for the valence band offset ΔE_v is given by

$$\Delta E_v = \Delta E_{VBM-1} - \Delta E_{VBM-2} - \Delta E_{core} \qquad (1)$$

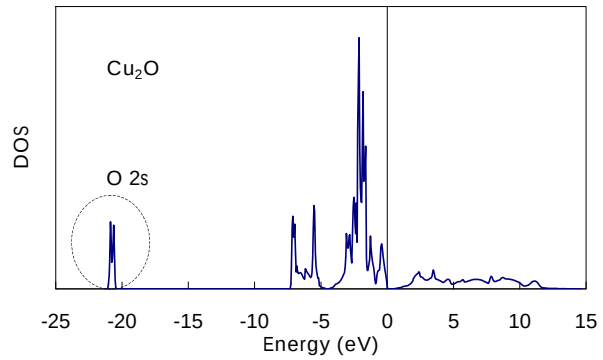
where ΔE_{VBM-1} (ΔE_{VBM-2}) is the energy separation between the valence band maximum VBM and the reference core level for Cu_2O (ZnO), and ΔE_{core} the difference in the core-level between Cu_2O and ZnO. The calculated densities of states for ZnO and Cu_2O are shown in Fig.2. In pseudopotential calculation, electrons in inner shells are not explicitly considered (except for the 3d orbitals in Cu and Zn, both of which are mixed into the valence band). The results shown in Fig.2 indicate that the O2s orbital forms a narrow band well separated from the upper band, and thus may be regarded as the inner core. Therefore, the local density of states was calculated for each oxygen atom in the supercell, and the O2s level (the peak energy of the density-of-states of the O2s band) was used as the reference core level in eq.(1) to calculate ΔE_v.

Results and Discussion

The circles in Fig.3 shows the calculated O2s levels for the respective O-atom layers in the supercells. Layer 0 and Layer 6 correspond to the interface. Fig.3(a) is based on supercell (a) in Fig.1, and Fig.3(b) is based on supercell (b).The origin of the energy scale is the Fermi energy for the respective

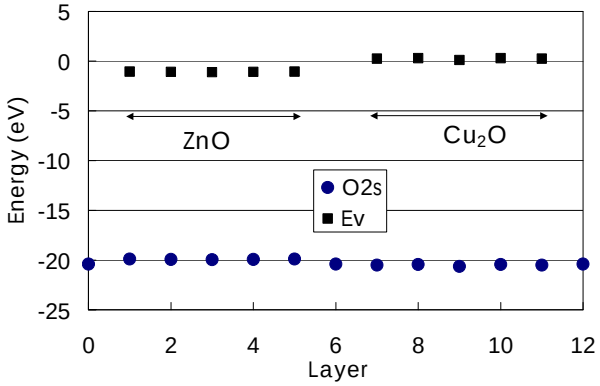


(a)

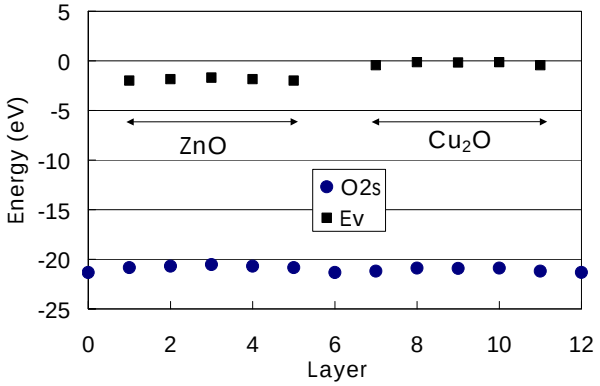


(b)

Fig. 2 Calculated densities of states for (a) ZnO and (b) Cu_2O.



(a)



(b)

Fig. 3 Calculated O2s levels and predicted VBM positions for the respective layer in the supercells. (a) is for supercell (a) in Fig. 1, and (b) for supercell (b).

sturucture. As shown in the figure, the O2s level is only weakly dependent on the atom position. The squares in Fig.3 shows the predicted VBM position for both the ZnO and Cu_2O layers, which were obtained assuming that the energy difference between the O2s level and the VBM are conserved (as in eq.(1)). ΔE_v was evaluated using the VBM energies averaged in the respective layers. ΔE_v =1.3eV for supercell (a) and ΔE_v=1.6eV for supercell (b). The predicted band alignment is schematically shown in Fig.4. The conduction band minimum CBM is higher for Cu_2O, and the conduction band offset ΔE_c= 0.1eV when supercell (a) is used and ΔE_c= 0.4eV when supercell (b) is used.

As noted in Introduction, the band offset has not been experimentally determined for ZnO/Cu_2O, to our knowledge. In refs. 3 and 4, ΔE_c was estimated from the electron affinity of each compounds. According to those previous estimates, the CBM is higher for Cu_2O, and ΔE_c is 0.8eV in ref.3 and 1.0eV in ref.4. Thus, the estimate using electron affinity gives a larger conduction band offset than the prediction based on the first-principle calculation.

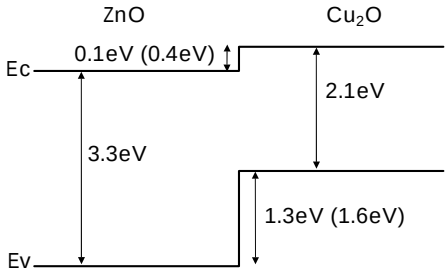


Fig. 4 Schematic of the predicted band alignment for ZnO/Cu_2O.

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