First Principles Calculation Study of Zn_{1-x}Mg_xO/Cu_2ZnSnS_4 Heterointerface

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Abstract. Cu_2ZnSnS_4 (CZTS) has attracted a lot of attention recently as a promising absorber layer material in a heterojunction solar cell. In this work, the Zn_{1-x}Mg_xO material is substituted for CdS due to its abundant and non-toxic consisting elements. We have studied the band gaps of Zn_{1-x}Mg_xO alloys with different values of x and the band offsets at Zn_{0.75}Mg_{0.25}O/CZTS heterointerface based on the first-principles and pseudopotential calculation method. The band gaps enhance linearly with the increasing values of x. The total density of state and local density of state of each atom in Zn_{0.75}Mg_{0.25}O/CZTS supercell are calculated. We predict that the heterojunction of Zn_{0.75}Mg_{0.25}O/CZTS is a type II heterointerface with a 0.2eV of conduction band offset, during which the conduction band minimum of Zn_{0.75}Mg_{0.25}O is lower than that of CZTS.

1. Introduction

Up to now, Cu_2ZnSnS_4 (CZTS), an up-and-coming candidate of absorber layer in thin film solar cells, has attracted much attention, owing to its direct and optimal band gap (1.5eV), high optical absorption coefficients in the visible region (10⁶cm⁻¹) as well as the abundance and the non-toxicity of all its constituents[1,2]. In 1996, the H. Katagiri research team in Japan produced the first CZTS solar cell, however, its efficiency was only 0.66%. The efficiency of CZTS and Cu_2ZnSn(Se, S)_4 (CZTSSe) solar cells has been continuously updated, which has reached to 9.4% and 12.6%[3, 4]by now, respectively. It greatly encourages the research in this field.

As is well known, CdS is usually employed as a buffer layer in CZTS-based thin film solar cells. But the existence of toxic element and small band gap restrain its development. Zn_{1-x}Mg_xO made up of is a n-type material, and the variable $E_g$ of Zn_{1-x}Mg_xO is larger than that of CdS, thus decreasing the abundant and nontoxic elements absorption loss at the short wavelength[5,6]. Therefore, it is expected to be a good substitute for CdS material.

The band alignment at window-absorber interface is one of the most important parameters. And it is often employed in assessing some important interface effects, i.e., quantum confinement and carrier transport, in particular, for the design of solar cells and other optoelectronic devices. It is generally believed that the conduction band minimum (CBM) of the p-type absorber layer is lower than that of the n-type window layer at the type-I interface, with a favorable moderate barrier height (smaller than 0.3eV)[7]. The increasing interface recombination and decreasing open circuit voltage are caused by the unfavorable CBM position at the CdS/CZTS heterointerface, during which the CBM of CZTS is
higher than that of CdS[8].

In this article, the effect of Mg component on the photovoltaic performance is predicted by calculating the band offsets at Zn$_{1-x}$Mg$_x$O/CZTS heterointerface with different Mg components. By changing Mg content (x), the moderate barrier height at the Zn$_{1-x}$Mg$_x$O/CZTS heterointerface is obtained.

2. Calculation Methods

The supercell of the (001) Zn$_{1-x}$Mg$_x$O/CZTS heterostructure is displayed in Figure 1. CZTS has a kesterite structure. And we assume that Zn$_{1-x}$Mg$_x$O has the cubic crystal structure. In the process of calculation, the average value of lattice constants of CZTS and Zn$_{1-x}$Mg$_x$O bulk materials is used for the lattice constant along the heterointerface. It is supposed that the lattice spacing in the perpendicular direction is the same in the respective bulk materials. The density of states (DOS) is calculated by using first principles calculation software package of PHASE code developed by Institute of Industrial Science, University Tokyo[9]. The generalized gradient approximation is used for the exchange correlation interaction[10].

The energy separation between the valence band maximum (VBM) and reference core levels were obtained firstly from the DOS of Zn$_{1-x}$Mg$_x$O and CZTS. The difference of core levels was achieved secondly from the band structure of the (001) Zn$_{1-x}$Mg$_x$O/CZTS supercell. The valence band alignment and conduction band alignment were gained as follows[11,12]

\[
\Delta E_v = \Delta E_{VBM}^{CZTS} - \Delta E_{VBM}^{Zn_{1-x}Mg_xO} - \Delta E_{core}^{Zn_{1-x}Mg_xO/CZTS}
\]

\[
\Delta E_c = |\Delta E_g - \Delta E_v|
\]

where $\Delta E_{VBM}^{CZTS}$ ($\Delta E_{VBM}^{Zn_{1-x}Mg_xO}$) is the energy separation between the core levels and VBM for the CZTS (Zn$_{1-x}$Mg$_x$O) material, $\Delta E_{core}^{Zn_{1-x}Mg_xO/CZTS}$ is the energy difference between core levels in the Zn$_{1-x}$Mg$_x$O/CZTS superlattice. This equation is based on the idea that the energy difference between the core levels and VBM in the respective bulk materials is conserved in the heterostructure. $\Delta E_g$ is the difference of band gap between CZTS and Zn$_{1-x}$Mg$_x$O bulk materials.

Figure 1. Supercell structure of (001) Zn$_{1-x}$Mg$_x$O/CZTS heterojunction.
3. Results and Discussion

3.1 Band gap and bowing parameter of Zn$_{1-x}$Mg$_x$O

The calculated total density of states for cubic structures of Zn$_{1-x}$Mg$_x$O are shown in Figure 2. The zepoint energy is taken as VBM. The states near VBM are primarily consist of Zn-3d and O-2p orbitals, and the conduction band minimum is composed of Zn-4s orbitals. We could see the energy level of O-2s and Zn-4s orbitals shift toward the higher energy with the increasing of Mg content in Zn$_{1-x}$Mg$_x$O alloys. The obtained energy band gaps are $E_g$, ZnO = 0.28 eV and $E_g$, ZnO = 2.92 eV, obviously less than experimental values (3.4 eV and 7.8 eV)[13]. This is because of the restriction of DFT, but it has less effect on the investigated electronic structure in the present work.

The Mg composition dependent energy band gap $E_g(x)$ for bulk Zn$_{1-x}$Mg$_x$O alloy can be expressed by using Vegard’s law[14]

$$E_g(x) = xE_g(MgO) + (1 - x)E_g(ZnO) - bx(1 - x)$$

(3)

Where $E_g(MgO)$ and $E_g(ZnO)$ are the energy band gaps for MgO and ZnO materials, respectively, and b is the band gap bowing parameter. Although the obtained values of band gaps are less than the experimental values, the error of band gap bowing parameter b is small in Eq. 3. It is because that the systematic band gap error cancels out in deriving the bowing parameters by comparing chemically identical systems in two different forms (MgO and ZnO)[15]. It has been confirmed in many documents[15, 16]

![Densities of states (DOS) for Zn$_{1-x}$Mg$_x$O with different Mg compositions (x values of 0, 0.125, 0.25, 0.375, 0.5 and 1).](image)

Table 1. Calculated band gaps (eV), bowing coefficient b (eV) and predicted band gaps (eV) for Zn$_{1-x}$Mg$_x$O alloys with different Mg compositions.

| Mg composition x | 0.125 | 0.25 | 0.375 | 0.5 | 0.625 | 0.75 |
|------------------|-------|------|-------|-----|-------|------|
| Band gap         | 0.56  | 0.78 | 1.08  | 1.35| 1.28  | 1.92 |
| Bowing parameter b | 0.4571| 0.8533| 0.8107| 1   | 2.77  | 1.8133|
| Predicted band gap | 3.9   | 4.34 | 4.86  | 5.35| 5.5   | 6.34 |
Table 1 shows the calculated band-gaps and bowing coefficients for Zn$_{1-x}$Mg$_x$O ternary alloys as a function of different Mg compositions (x values). The calculated values of band gaps are 0.28 eV, 0.56 eV, 0.78 eV, 1.08 eV, 1.35 eV, and 2.92 eV with different x values of 0, 0.125, 0.25, 0.375, 0.5, and 1, respectively. And we also calculate the band gaps of Zn$_{1-x}$Mg$_x$O alloy at different concentration by using the bowing parameters and value of experimental band gaps ($E_{g, ZnO}$=3.4 eV, $E_{g, MgO}$=7.8 eV). The results are presented in Table 1, the band gaps almost increase linearly with the increase of the x values. This is due to the energy of Zn-4S orbital shifting toward the higher energy level with the increase of Mg content. This trend is also consistent with other investigation[17].

3.2 Band offsets for Zn$_{0.75}$Mg$_{0.25}$O/CZTS heterointerfaces

The core level energies of respective layer in the Zn$_{0.75}$Mg$_{0.25}$O/CZTS supercell were revealed in Figure 3. The ‘‘Ev’’ energies marked by the stars demonstrated the VBM positions for both Zn$_{0.75}$Mg$_{0.25}$O buffer layer and CZTS absorber layers. The calculated ∆Ev from the averaged VBM energy is 3.0 eV and CBM of Zn$_{0.75}$Mg$_{0.25}$O layer is lower than that of CZTS layer, i.e., the Zn$_{0.75}$Mg$_{0.25}$O/CZTS heterojunction belongs to type II interface. The band offset of Zn$_{0.75}$Mg$_{0.25}$O/CZTS heterointerface is displayed in Figure 4. For Zn$_{1-x}$Mg$_x$O alloys, the position of conduction band minimum varies with the change of Mg compositions, while the position of VBM is almost constant. It is reported that when the band gap of CZTSSe is 1.15 eV, the conduction band offset is zero at CdS/CZTSSe interface, while the conduction band minimum of ZnO is 0.4 eV lower than that of CdS[18], which is consistent with our prediction. As shown in Figure 4, the heterojunction of Zn$_{0.75}$Mg$_{0.25}$O/CZTS is a type II heterointerface with a 0.2 eV of conduction band offset, during which the conduction band minimum of Zn$_{0.75}$Mg$_{0.25}$O layer is lower than that of CZTS layer. For the type II heterointerface, there are not formed barrier for the photoexcited electrons crossing the interface. But the band bending is reduced by ∆Ec. It plays an important role in an increase of the recombination rate for majority carriers at the interface.

Figure 3. Calculated energy levels and predicted VBM positions Ev for the respective layers in the (001)Zn$_{0.75}$Mg$_{0.25}$O/Cu$_2$ZnSnS$_4$ supercell.
4. Conclusions

In this work, we have studied the band gap of Zn$_{1-x}$Mg$_x$O alloy with different values of $x$ and the band offsets at Zn$_{0.75}$Mg$_{0.25}$O/CZTS heterointerface based on the first-principles, pseudopotential calculation method. The energy band gaps increase linearly with the increase of Mg components. And the heterojunction of Zn$_{0.75}$Mg$_{0.25}$O/CZTS is a type II heterointerface with a 0.2 eV of conduction band offset, during which the conduction band minimum of Zn$_{0.75}$Mg$_{0.25}$O is lower than that of CZTS.

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