

# The study of electronic structure and absorption coefficient of ZnTe:O alloys: A GGA+U method



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## ABSTRACT

In this study the electronic structures and absorption coefficient for highly mismatched ZnTe<sub>1-x</sub>O<sub>x</sub> alloys have been investigated on the basis of the GGA+U approximation. It is found that an isolated intermediate band (E<sub>-</sub>) is formed within the band gap of ZnTe by the incorporation of low content of O ( $x < 0.0625$ ) into ZnTe. In the range of the low O content, the variation of E<sub>-</sub> and E<sub>+</sub> is in agreement with the theoretical prediction by the well-known band anti-crossing model. As the O content  $x$  exceeds 0.0625, the E<sub>+</sub> energy position decreases and intermediate band (E<sub>-</sub>) cannot exist in isolation states, which is consistent with the experimental results but in contrast to the band anti-crossing model. The chemical bonding pictures show that the intermediate band states are mainly caused by the antibonding states that are formed through the hybridization of a localized O 2s state and some localized Zn 3d4s4p states. The calculated absorption coefficient exhibits an obvious enhancement within the ZnTe:O bandgap, which indicates the formation of intermediate states can effectively make use of low energy photons to improve the conversion efficiency of final solar cell based on ZnTe:O materials.

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## 1. Introduction

The next generation of solar cells requires not only low cost but high conversion efficiency. The thin film technology has greatly reduced the production cost of the solar cells nowadays, and the improvement of conversion efficiency becomes especially prominent toward the future development of solar cells. To exceed the Shockley–Queiser limit for single-junction solar cell, many efforts both from the research and industrial communities have been made to design novel structures or search for new photovoltaic materials. The multi-junction solar cells connected in series using III–V semiconductors on Ge substrates have been realized with the recorded efficiency up to 45% have been realized, and however, the challenges lie in strict materials with lattice match and current match of each cells [1–3]. The fabrication process is much complex and expensive. Alternatively, the concept of intermediate band solar cell (IBSC) has recently attracted renewed attention to achieve high power conversion efficiency. According to prediction of the detailed balance theory, a single-junction cell with an

intermediate band could reach photoelectric conversion efficiencies of 62% [4] and 71.7% [5].

Highly mismatched alloys (HMAs) such as GaAs:N and ZnTe:O have been employed as an active absorption layer to demonstrate the concept of IBSCs [6–8]. The replacement of group V (VI) elements by the isoelectronic N (O) in III–V (II–VI) compound semiconductors, leads to the formation of a novel type of alloys named highly mismatched alloys (HMAs). The substitution of high electro-negativity atom will induce a bound state energy level formed in the band gap of highly mismatched alloys (HMAs). The bound state energy level related of the high electro-negativity impurities within the band gap of the compound semi-conductor is generally considered as intermediate band (IB), which can improve absorption of photons with energies lower than the band gap. Therefore, the HMAs with intermediate band (IB) used as absorb-layer will lead to an increase in short circuit current without losing the open circuit voltage, which is an important way to enhance efficiency of solar cell.

Although the proposed intermediate band solar cells are very promising, the progress on intermediate band solar cells is still limited due to several scientific and technological challenges. Firstly, a limited solid solubility of higher electro-negativity elements in HMAs is difficult to be pushed. Secondly, it is also difficult

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to control defect states in HMAs. Most importantly, there are still many fundamental questions far from understanding for HMAs. For instance, the electronic structures and the physical mechanisms of intermediate band are still under investigation. The optical transition strengths of IB to both valence band (VB) and conduction band (CB) are lack of study, although it is crucial to determine the device performance of IBSC.

In this work, we employ density functional theory (DFT) to calculate the electronic structures and absorption coefficient of  $\text{ZnTe}_{1-x}\text{O}_x$  highly mismatched alloys with a large oxygen component range varying from 0 to 0.25. The comprehensive analysis to the effect of incorporated O on band structures and density of states in  $\text{ZnTe}:\text{O}$  have been discussed with comparison to the experimental studies and theoretical predictions by band anti-crossing model. The variation of optical transition strength related to IB has been also investigated.

## 2. Computation details

All the calculations have been carried out by density functional theory (DFT) [9] using the Vienna ab initio simulation package (VASP) 5.3.3 [10]. The generalized gradient approximation (GGA)+U method [11–13] with the Perdew–Becke–Ernzerhof (PBE) exchange correlation function [14] was employed to calculate the on-site Coulomb correlation for the Zn 3d and O 2p electrons to obtain the proper band gap value. The plane wave basis set has been included and truncated with cut-off energy of 400 eV. According to the methods mentioned above, a  $5 \times 3 \times 5$  Monkhorst–Pack [15] grid and 38 K points in the irreducible Brillouin zone were employed for  $\text{ZnTe}$   $2 \times 3 \times 2$  super-cell structure optimization. The band structures of zinc-blende (ZB)  $\text{ZnTe}_{1-x}\text{O}_x$  super-cells were obtained along the path of L (0.5,0.5,0.5)-G (0.0,0.0,0.0)-X (0.5,0.0,0.5) in the first Brillouin zone.

It should be pointed out that as one of Te atoms is substituted by an O atom in  $\text{ZnTe}$  super-cell, the O atom is tetrahedrally surrounded by four equivalent Zn atoms, which is similar with the situation of O in ZB- $\text{ZnO}$ . Therefore, electronic band structure and electrical property of intrinsic ZB- $\text{ZnO}$  has been calculated as a reference, which is good to establish the relationship between the IB formation mechanism and impurity states related to O elements. Moreover,  $\text{O}_{\text{Te}}$  is more stable than other types of O defect in  $\text{ZnTe}$  according to Ling's formation energy calculation of the other types of isolated oxygen defects [16]. With the substitutions of  $\text{O}_{\text{Te}}$  increasing, they are energetically favorable to get together and to form  $\text{Zn-O}_{\text{Te}}$  clusters, which is very similar with the Zn–O bonding in ZB- $\text{ZnO}$ . These calculated results are consistent with Ling's findings obtained by the bonding orbital analysis [16].

It is well known that  $\text{ZnO}$  is a transition metal oxide, a strongly correlated material system and thus, the standard density functional theory (DFT) method always underestimates its band gap. Here, a GGA+U method is used to treat the strong on-site Coulomb interaction of localized electrons, which is not correctly described by ordinary DFT method. The on-site Coulomb interactions are particularly strong for localized d and f electrons and also exhibit non-negligible effect to localized orbitals of p electrons in wurtzite  $\text{ZnO}$  [17,18].

Therefore, in ZB- $\text{ZnO}$ , the Hubbard  $U$  terms for Zn 3d ( $U_{\text{Zn}}$ ) and the O 2p ( $U_{\text{O}}$ ) electron states were established by adjusting the band gap and the energy levels of the Zn-3d close to experimental values. The dependence of the band gap and Zn 3d energy levels on both  $U_{\text{Zn}}$  and  $U_{\text{O}}$  has been shown in Fig. 1. It is found that the band-gap of Zinc blend- $\text{ZnO}$  increased with the increment of  $U$  values for both Zn and O and approach to the experimental value (3.37 eV at room temperature) when  $U_{\text{Zn}} = 11.2$  eV and

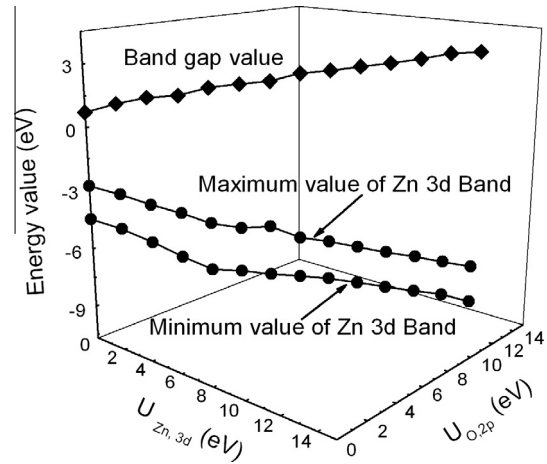


Fig. 1. Dependence of the band gap ( $E_g$ ) and Zn 3d band of ZB- $\text{ZnO}$  on Hubbard  $U$  of Zn 3d and O 2p.

$U_{\text{O}} = 11.2$  eV [19–21]. Choosing the  $U_{\text{Zn}}$  values in ZB- $\text{ZnTe}$ , the maximum energy levels of the Zn-3d energy band is close to  $-10$  eV, which is consistent with the results obtained by Karazhanov et al. [22]. Although the calculated band gap value of 2.13 eV by GGA+U method is still a bit smaller than the experimental value (2.29 eV), it is more reasonable than the GGA calculated band gap value (1.06 eV). Besides, Hubbard  $U$  has been imposed on the Te 5p states, and it hardly further improved the energy gap of  $\text{ZnTe}$ . It is because that the Coulomb correlation effects between p electrons and 3d electrons are more pronounced in  $\text{ZnO}$  than  $\text{ZnTe}$  [22]. Therefore, the IB properties of  $\text{ZnTe}_{1-x}\text{O}_x$  alloy are calculated with the tested Hubbard  $U$  parameters ( $U_{\text{Zn}} = 11.2$  eV,  $U_{\text{O}} = 11.2$  eV and  $U_{\text{Te}} = 0$  eV).

## 3. Results and discussion

### 3.1. Electronic structures

#### 3.1.1. The properties of energy band structure

The band structures of  $\text{ZnTe}_{1-x}\text{O}_x$  as a function of O content ( $x = 0.0208, 0.03125, 0.0625, 0.09375$  and  $0.125$ ) have been studied as shown in Fig. 2. In comparison, the energy band structures of intrinsic ZB- $\text{ZnTe}$  supercell, taken as reference material, have also been computed by the methods of GGA+U and shown in Fig. 2(b). According to band anti-crossing model [6–7,23], as the high electro-negativity O element is incorporated in  $\text{ZnTe}$ , an anti-crossing interaction makes the conduction band bottom splitting into two subbands of  $E_-$  and  $E_+$ . It described that the interaction is mainly from anti-crossing property of both the conduction band bottom and localized O impurity states in  $\text{ZnTe}_{1-x}\text{O}_x$  alloys and the relationship of both  $E_-$  and  $E_+$  can be written into following equation [6–7,23]:

$$E_{\pm} = \left( E_a + E_b \pm \left[ (E_a + E_b)^2 + 4C_{ab}^2 x \right]^{1/2} \right) / 2 \quad (1)$$

where  $E_a$  is the energy level of O impurities and  $E_b$  is the minimum of conduction band of  $\text{ZnTe}$  referred to the valence band maximum, and  $C_{ab}$  is the coupling coefficient between the conduction band states and localized O impurities states.

Fig. 2 shows the energy band structure of the  $\text{ZnTe}_{1-x}\text{O}_x$  ( $x = 0.0208$ ) alloy and the  $\text{ZnTe}$ . Comparing the energy band structures of  $\text{ZnTe}_{1-x}\text{O}_x$  ( $x = 0.0208$ ) alloy to that of  $\text{ZnTe}$ , we can clearly find that the conduction band bottom splits into two sub-bands ( $E_-$  and  $E_+$ ), when the higher electro-negativity O element is incorporated in  $\text{ZnTe}$  as shown in Fig. 2(b). The formation of two

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