Theoretical Study on the Electronic and Structural Properties of p-Type Transparent Conducting Metal Oxides

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1. Introduction

Transparent conducting oxides (TCOs) have been extensively used as transparent electrodes in optoelectronic devices, solar cells, and organic light-emitting diodes, pixel electrodes in devices such as liquid-crystal displays, and as touch screen in transparent windows [1]. More recently, they have become the subject of intense academic and industrial investigation for applications as transparent electrodes in photovoltaic solar cells, flat panel displays, and light emitting diodes. However, the high cost of raw material and chemical stability in some device structures limit the potential applications of *n*-type TCOs. On the other hand, *p*-type TCOs have conductivities 3-4 orders of magnitude lower than their n-type counterparts.

If *p*-type materials with high conductivities and transparencies could be manufactured industrially, a variety of new applications would open up, including p-nhetero-junctions, transparent diodes, transparency transistors, and functional windows. Recently, the Zn-doped In_2O_3 (IZO) system has been attracting much attention due to a larger work function and a wide transmittance window from 400 to 2500 nm [2]. Kawazoe et al. [3] have reported that the *p*-type TCO is considered to originate from a general characteristic in the electronic structure of the metal oxides; the strong localization of the upper edge of the valence band to the oxide ions. Therefore, the electronic structure is important for understanding the properties of the metal oxides. However, a comprehensive investigation on the electronic structure of the Zn-doped In₂O₃ system with different composition is lacking.

In the present study, we undertook theoretical work on doping with acceptors by our original tight-binding quantum chemical molecular dynamics program, "Colors" and the density functional theory (DFT) method. The role of the Zn-dopant, the structural features, electronic and electrical properties and the source of the carrier concentration were firstly reported.

2. Computational Methods

First-principles DFT calculations were performed by DMol³ program [4] under the periodic boundary condition

so as to investigate the electronic properties of IZO. The basis sets of double numerical plus polarization functions (DNP) were used. Effective core potentials were used for indium and zinc below the 3d, 4d and 5s orbitals.

The calculations were performed using the Vosko-Wilk-Nusair local exchange-correlation functional (LDA). The thermal smearing was applied to orbital occupation to accelerate SCF convergence of band calculations. Moreover, in order to get the information of electrical properties, the program "Colors" [5] was used for the present calculations.

3. Results and Discussion

IZO with different doping position has been calculated by using DFT method. In the present study, we employed an In_2O_3 crystal structure constituted of 32 indium and 48 oxygen atoms with a lattice constant of 10.12 Å. The cubic bixbyite (In_2O_3) crystal structure has two types of sixfold-coordinated In^{3+} sites, which are referred to as "*b*-site" and "*d*-site".

The eight *b*-sites have six equidistant oxygen neighbors, while the twenty-four *d*-sites are coordinated to six oxygen atoms at three different distances. Due to the complex geometry of In_2O_3 , there are various doping possibilities for Zn. According to the described structure of In_2O_3 and the experimental optimum concentration of 7wt%[6] (two zinc atoms in IZO model), the IZO model with one *b*-site Zn²⁺ and one *d*-site Zn²⁺ was constructed. Fig.1 shows the optimized geometry of non-doped In_2O_3 (a) and Zn-doped In_2O_3 (b).

(b)



Fig. 1 The structure of: (a) $In_{32}O_{48}$, and (b) $In_{30}Zn_2O_{48}$. White sphere=O, gray=In. and black=Zn.

(a)

Based on the optimum geometry of IZO, the effect of Zn-dopant on electronic properties of n-type In₂O₃ was investigated by DFT method. Fig. 2 shows the calculated band structures for non-doped In₂O₃ (a), and the enlarged upper region of the valence band of non-doped In₂O₃ (b). In addition to non-doped In₂O₃, the obtained band structures of Zn-doped In_2O_3 (a) and the enlarged upper region of the valence band of Zn-doped In_2O_3 (b) were shown in Fig. 3. It is clear from Fig. 2 (a) and Fig. 3(a), the lower region of the conduction band is still keeping the similar electronic structure while in comparison with the enlarged upper region of the valence band of non-doped In₂O₃, an dopant level was observed just above the upper region of the valence band of Zn-doped In₂O₃. The appearance of this new feature would explain the reason of p-type conductivity.



Fig. 2. The band structure of: (a) non-doped In_2O_3 , (b) the enlarged upper region of the valence band of non-doped In_2O_3 .

In order to identify the properties of the new feature, molecular orbitals were calculated by DFT method. Fig. 4 depicts the molecular obitals diagrams for the upper region of the valence band (a), the acceptor level (b), and the lower region of the conduction band of Zn-doped $In_2O_3(c)$. According to the molecular orbital diagram between the impurity and surrounding oxygens, which is shown in Fig. 4 (a), the bands at the upper region of valance band are mostly composed of anti-bonding molecular orbital of Zn (3d) and O (2p), while the bands at the lower region of the conduction band contribute to delocalized O (2s) orbital, Fig. 4(c). The energy difference between the upper region of the valence band and the acceptor level is 0.08 eV. Therefore, the acceptor level was found just above the upper region of the valence band, which indicates that IZO model has *p*-type semiconductor characteristics. Fig. 4 (b) shows that acceptor level is also composed of un-occupied anti-bonding molecular orbital of Zn (3d) and O (2p), and has the similar orbital shape with the upper region of the valence band. Moreover, the electrical properties of IZO



Fig. 3. The band structure of: (a) Zn-doped In_2O_3 , (b) the enlarged upper region of the valence band of Zn-doped In_2O_3 .



Fig. 4. Molecular orbital diagrams. (a) Upper region of the valance band, (b) acceptor level and (c) lower region of the conduction band.

calculated by "Colors" program will be reported in the conference.

4. Conclusions

In the present study, theoretical method was used to challenge the study on the electronic structure of p-type of In_2O_3 for the first time. As a result, it has became clear that due to the existence of the substituted Zinc atom and the impurity states can be formed leading to the increase of conductivities of ITO.

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