Ab initio studies of the Sn-doped ZnO transparent conductive oxide

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Abstract. Based on density functional theory within the generalized gradient approximation, Sn-doped wurtzite ZnO transparent conducting oxide (TCO) was investigated, where structures relaxations, formation energies, and electronic structure of Sn doped in ZnO are studied. It was found that the lattice parameters of the Sn-doped ZnO increased with increasing Sn concentration. The substitutional Sn (Sn\textsubscript{Zn}) atom has low formation energy and introduces impurity levels below the conduction band minimum. Also, substitutional Sn atoms contribute significantly delocalized s orbitals in the conduction band states, which are expected to increase the conductivity of the material. Additionally, with increase of Sn concentration, the band gap is narrowed. We further identify that the lower concentration of heavily doped of Sn, the conductivity of ZnO is stronger. The calculated results are helpful to gain a systematic understanding of structure, electrical properties of Sn-doped ZnO transparent conducting oxide.

1. Introduction
Znixcide (ZnO) has owned many features, including optical, semiconducting, piezoelectric, electro-optic, and optoelectronic properties. Because of wide band gap (3.4 eV) and larger binding energy (60 meV), ZnO can be used in many fields, such as light appliance, solar cell, sensors, actuators, flat panel liquid crystal monitor, and infrared reflector [1]. It is well known that pure-ZnO is polar semiconductor, demonstrating as n-type, and it has usually low conductivity. In order to gain transparent conducting oxide materials, it should employ doping donor elements to improve the conductivity such as Al [2-4], Ga [5], In [6]. For Al doped ZnO, on experiment, Al doping ZnO could lower the resistivity of ZnO [2-4], lower Madelung energy [7], improve the electrical conductivity, and its optical absorption edge blue-shifted [8], which can gain good quality TCO. In theory, Zhang et al. [9] have calculated the electronic structure and optical properties of ZnO in different Al doping, showing that AZO materials can used as excellent transparent conducting films. Recent, many groups have chosen Sn as the dopant in ZnO. Seval Aksoy et al. [10] have reported that the undoped and Sn doped ZnO films were deposited by a spray pyrolysis method onto the glass substrates, and suggested that the absorption edge shifts to the lower wavelengths with Sn dopant. Benelmadjat et al. [11] proposed sol-gel method to investigate the effects of Sn dopant on structural and optical properties. It shows an important effect of Sn dopant on optical band gap. Saliha et al. [12] reported that Sn doped ZnO films have been deposited by sol gel spin coating method. They investigated the effect of Sn

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incorporation on structural and electro-optical properties of ZnO films. They observed that the shift of absorption edge is associated with shrinkage effect and the electrical conductivity of the ZnO film enhanced with the Sn dopant. Li et al. [13] reported that Sn-doped ZnO microrods have been fabricated by a thermal evaporation method. They investigated the effect of Sn dopant on the microstructure, morphological and composition of as-prepared Sn-doped ZnO microrods. Sn doping of ZnO films have been widely reported to investigate the influence of doping on the structural and optical properties. K.C.Yung et al. [14] have proposed that the optical band gap in free standing transparent ZnO films using the sol-gel method can narrow with the dopant of Sn. They found that the optical band gap of Sn-doped ZnO is red-shifted due to the deep states in the band gap. It is well known that using the higher valence of dopants is mainly to provide more free electrons, which leads to lower the impurity doping and improve the quality and optical properties of thin films [15]. However, there are few studies about the electronic structure and the effects of Sn concentration of ZnO from the theoretical calculation using the first principles. In this work, the paper is organized as follows: Firstly, the computational methods are introduced. Then, the formation energy and electronic structure of Sn0.0625Zn0.9375O are calculated, and finally, the effects of concentration of Sn dopant on electrical properties of ZnO are considered by the first principles.

2. Computational methods

All calculations were carried out using the density functional theory with the generalized gradient approximation (GGA) and the projector augmented wave (PAW) pseudo-potentials, as implemented in the VASP codes [16,17]. A gamma centred 5x5x3 k-point mesh for the Brillouin zone was employed. The energy cutoff is 450 eV. We have constructed the four configurations, which are listed as follows: Configuration (a): 2x2x2 (pure-ZnO), Configuration (b): 2x2x2 (Sn0.0625Zn0.9375O), and Configuration (c): 2x2x3 (Sn0.0417Zn0.9583O), Configuration (d): 3x3x2 (Sn0.0278Zn0.9722O). All the atoms have been relaxed until the force on each atom was below 0.01 eV/Å. By optimizing the geometry of the pure-ZnO, the calculated lattice parameters were got as follows: a= 0.328 nm, b= 0.328 nm, c= 0.527 nm, c/a= 1.608. They were consistent with experimental results [18]: a= 0.324 nm, b= 0.324 nm, c= 0.519 nm, c/a= 1.602. The calculated parameters are in excellent with the experiment results, indicating that our calculation methods are reasonable. We have mainly considered the formation energy (E_f(D,q)) for a complex with a defect D at charge state q. Calculated the formation energy of Sn substituted Zn site and Sn substituted O site. The calculation equation can be calculated as [19]

\[
E_f(D,q) = [E_{tot}(D,q) - E_{tot}(ZnO)] + \sum_i n_i \mu_i + q(E_F + E_{VBM})
\]

(1)

\[
E_{tot}(ZnO) = \mu_{Zn} + \mu_O
\]

(2)

where \( E_f(D,q) \) is the defect formation energy for the studied supercell. \( E_{tot}(D,q) \) is the total energy of a supercell containing the defect D at the charge state q. \( E_{tot}(ZnO) \) is the energy of the pure ZnO in the same supercell. \( E_F \) is the Fermi energy level with respect to the VBM of the host, which varies up to the experimental value of 3.4 eV. \( E_{VBM} \) is the valence band maximum of the pure ZnO. \( \mu \) is the chemical potential of the elements. \( \mu_i \) is the chemical potential of atom i referenced to the element. \( \mu_i (bulk) \) is the energy of the bulk material. The chemical potentials of Zn and O satisfy the following equations:

\[
\mu_O^{min} = E_{tot}(ZnO) - \mu_{Zn} (bulk)
\]

(3)

\[
\mu_{O}^{min} = E_{tot}(ZnO) - \mu_{O}(O_2)
\]

(4)
And the chemical potential of Zn is the energy of Zn bulk. The chemical potential of O is the half energy of oxygen.

3. Results and discussion

3.1. Electronic structure of \( \text{Sn}_{0.0625}\text{Zn}_{0.9375}\text{O} \)

Firstly, we have calculated the formation energies of Sn occupied Zn site (\( \text{Sn}_{\text{Zn}} \)) and Sn occupied O site (\( \text{Sn}_{\text{O}} \)). The results are listed as Table 1, from which it can be found that the formation energy of \( \text{Sn}_{\text{Zn}} \) is less than that of \( \text{Sn}_{\text{O}} \). It means that Sn occupied Zn may be the most stable doping way among all the related defects. This is also in excellent consistent with the experiment [12].

| Formation energy /eV | \( E_f /eV \) |
|---------------------|----------------|
| Zn site             | 5.2421         |
| O site              | 11.6061        |

Table 1. Formation energy of ZnO for \( \text{Sn}_{\text{Zn}} \) and \( \text{Sn}_{\text{O}} \)

Sequentially, we can make a clear comparison of pure-ZnO and Sn doped ZnO with \( \text{Sn}_{0.0625}\text{Zn}_{0.9375}\text{O} \) (as shown in Fig. 1). All energies are relative to the respective Fermi energies. It shows that the Fermi level is located at the bottom of conduction band for Sn doped ZnO. Moreover, the valence bands and the conduction bands are both shifted into the lower energy. In addition, as the Sn is doping in ZnO, Sn supplies four electrons, while Zn provides two electrons. That is to say more free electrons are introduced into the doped systems. Therefore, it can be concluded that Sn is a good candidate for enhancing the electrical conductivity. The band gap of pure-ZnO is 0.76 eV (as shown in Fig. 2), which is lower than that of experiment value (3.4 eV), because of the well-known of GGA. Fig. 3 is the band structure of \( \text{Sn}_{0.0625}\text{Zn}_{0.9375}\text{O} \), from which we can see the band gap narrowed to 0.15 eV. It can be observed that Sn doped ZnO can narrow the band gap, which is demonstrates as red-shifted. This result agrees well with the experiment [14].

From PDOS of \( \text{Sn}_{0.0625}\text{Zn}_{0.9375}\text{O} \) show in Fig. 4, it can be seen an impurity peak near the Fermi level is formed, which is favorable for improve conductivity of ZnO. The upper conduction band within -0.96 to 0 eV is mainly contributed by Sn-s states near the Fermi level. However, the lower conduction band is constituted by Sn-p and Zn-s states. The valence bands are divided into two parts: the upper
valence band within -19.73 to -18.30 eV is introduced by O-s, and the lower valence band within -8.71 to -8.31 eV is introduced by Zn-d.

3.2. Effects of Sn concentration on conductivity of ZnO

From the Table 2, we can see that as increase of x, the lattice parameters of a and c are both increased. The calculated result agrees well with the experimental results [11]. It is well known that Zn ionic radius has almost the same as the Sn ion ($r_{Zn}^{2+} = 0.74 \text{ Å}$ and $r_{Sn}^{4+} = 0.69 \text{ Å}$) [20]. When Sn is incorporated to the ZnO film, Sn$^{4+}$ substitutes Zn$^{2+}$ site leads to two more free electrons to contribute to the electrical conductivity. So, Sn doping ZnO possibly can realize good conductivity. In Fig.5, we can see that the Fermi levels are all located at the bottom of conduction band of Sn$_x$Zn$_{1-x}$O. Moreover, the peak values of the impurity states are increased with the decrease of x near the Fermi level. In addition, it can be observed that the band gap becomes narrow with increase of x, due to the bottom of conduction band of gradually shifted to lower energy.

Table 2. Lattice parameters and band gap energy of Sn$_x$Zn$_{1-x}$O.

| Sn$_x$Zn$_{1-x}$O | a/Å  | c/Å  | c/a  | band gap energy / eV |
|-------------------|------|------|------|---------------------|
| 0                | 3.281| 5.277| 1.608| 0.76                |
| 0.0278            | 3.285| 5.309| 1.616| 0.46                |
| 0.0417            | 3.290| 5.311| 1.614| 0.27                |
| 0.0625            | 3.294| 5.354| 1.625| 0.15                |

To further discuss the effects of Sn concentration on electronic structure of ZnO, PDOSs of Sn$_x$Zn$_{1-x}$O are plotted in Fig.6a to 6d. It can be seen that the location of the valence band maximum is determined by O-p and Sn-s. Furthermore, with increase of x, the proportion of Zn is reduced, the peak value of O-p are increased near the Fermi level. It also can be observed that the conduction band is mainly depended on Sn-s, which plays an important role for ZnO high conductivity. As increase of x, the Sn-s shifts to the lower energy, which promote the band gap is narrow. And then red-shifted occurs.
However, the conductivity property of a semiconductor is not only dominated by the number of electrons, but also depends on the mean free time. According to the solid theory [21], mean free time
\[ \tau_i \cdot N_i^{-1/3} \]
Here, the calculated values of dopant concentration are 2.48404×10^21 cm⁻³, 1.6691147×10^21 cm⁻³, and 1.1957×10^21 cm⁻³ for Sn₀.₀₆₂₅Zn₀.₉₃₇₅O, Sn₀.₀₄₁₇Zn₀.₉₅₈₃O, and Sn₀.₀₂₇₈Zn₀.₉₇₂₂O, respectively. Obviously, for our first-principle calculations, Sn atoms are heavily doped in ZnO compared with experiment. The calculated numbers of electrons are 2.01842, 1.88004, and 1.69589 for Sn₀.₀₆₂₅Zn₀.₉₃₇₅O, Sn₀.₀₄₁₇Zn₀.₉₅₈₃O, and Sn₀.₀₂₇₈Zn₀.₉₇₂₂O. Due to the configurations are n-type semiconductor, the electronic conductivity can be computed as
\[ \sigma_i = \frac{n_i q^2 \tau_i}{m_e^*} \]
where \( m_e^* \) is the electron effect mass. \( n \) is the number of electrons. \( q \) is the charge state, and \( \tau \) is the free time on average. \( \sigma \) is the conductivity of the dopant system. Thus, the conductivity ratios of various complexes should be calculated. The conductivity of Sn₀.₀₆₂₅Zn₀.₉₃₇₅O, Sn₀.₀₄₁₇Zn₀.₉₅₈₃O, and Sn₀.₀₂₇₈Zn₀.₉₇₂₂O was set to be \( \sigma_1 \), \( \sigma_2 \), \( \sigma_3 \), respectively, and then the ratios are as follows:
\[ \frac{\sigma_2}{\sigma_1} = \frac{n_2 q^2 \tau_2 / m_e^*}{n_1 q^2 \tau_1 / m_e^*} = \frac{1.69589 \times 1.669114}{1.88004 \times 1.11957} = 1.3448, \]
\[ \frac{\sigma_3}{\sigma_1} = \frac{n_3 q^2 \tau_3 / m_e^*}{n_1 q^2 \tau_1 / m_e^*} = \frac{2.48404 \times 1.88004}{1.669114 \times 2.01842} = 1.3862. \]

Obviously, we can get: \( \sigma_3 > \sigma_2 > \sigma_1 \). It can be seen that the conductivity of Sn₀.₀₂₇₈Zn₀.₉₇₂₂O is larger than that of others. From the calculated results, we can see that the conductivity of Sn-doped ZnO is closely related to the concentration of impurities and the average number of electrons in the conduction band. And the concentration of impurities is depending on the free time on average. Therefore, we can draw a conclusion that the lower concentration of heavily doped Sn, the conductivity of ZnO is stronger.
4. Conclusions
The formation energy, geometry structure, and electronic structures of Sn$_x$Zn$_{1-x}$O have been calculated by the first principle method. The calculated results show that Sn$_x$Zn$_{1-x}$O has lower formation energy than that of Sn$_{1-x}$O, and the lattice parameters are both increased with the increase of x. We also found that the conduction band near the Fermi level is mainly determined by the Sn-s states near the Fermi level, and the band gap of Sn$_x$Zn$_{1-x}$O narrows, as the increase of x. Furthermore, the conductivity have been employing to compared, we can draw a conclusion that the conductivity of Sn$_x$Zn$_{1-x}$O decrease with the concentration of Sn increasing. The results are helpful to gain a systematic understanding of structure, electrical properties of Sn-doped ZnO TCO, and also can support and explain the experimental results.

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