Density Functional Theory Study on the Electronic Structure and Optical Properties of Sb-doped SnO$_2$

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Abstract  The electronic structures and optical properties of Sb-doped SnO$_2$ are studied by first principle calculation based on density functional theory (DFT). The computed results show that, with the increase of Sb doping concentration, the Fermi energy level passes through conduction band, and the band gap is narrower in succession, meanwhile, the energy level of shallow donor impurity is shifted away from the conduction band bottom, which makes the conductivity enhanced. The calculated results of charge density indicate that Sb-doping can change the property of SnO$_2$ bond formation, which makes the covalent weakened and the metallicity enhances with the increase of Sb doping concentration. The calculated results of optical properties show that the imaginary part of the dielectric function has a red shift like the total density of state (TDOS) with the increase of Sb doping concentration, which indicates the internal relationship between electronic structure and optical properties theoretically.

Key words  materials; SnO$_2$; Sb-doping; density functional theory; electronic property; optical property

1 Introduction

Stannic oxide (SnO$_2$), an n-type wide band-gap semiconductor, whose experimental band gap is 3.6 eV, has high exciton binding energy (130 meV in experiment)\cite{1}. The new materials formed by doped SnO$_2$ have higher conductivity and better optical transmittance, and the research on metallic ion doped SnO$_2$ compound has involved some electronic and optical theories and experimental discusses. Du et al\cite{2} calculated the electronic properties of III family doped SnO$_2$. Yu et al\cite{3,4} studied the density of states and optical properties of Al, N doped SnO$_2$. Lu et al\cite{5} investigated the electronic structure and optical properties of Fe-
doped SnO₂.

Stannic oxide conductive film SnO₂: Sb (ATO) has similar photoelectric properties with In₂O₃: Sn (ITO), whose research is mature, and ATO reserve is rich and low cost, so there are many studies about laboratory preparation and process improvement of ATO\(^{[6-8]}\). Guo et al\(^{[9]}\) studied the electrical and optical properties of sol−gel processing Sb−doped SnO₂ thin film by experimental measurement. Wang et al\(^{[10]}\) prepared SnO₂ B Sb thin films and studied its photoluminescence characteristics. Wang et al\(^{[11]}\) prepared SnO₂: Sb transparent conducting thin films by sol−gel method and studied its photoelectric properties.

Deng et al\(^{[12]}\) investigated the effect of Sb doping on electrical conductivity of SnO₂ by first−principle calculation. However, the reports about first principle simulative calculation of electronic and optical properties of Sb−doped SnO₂, especially high Sb doping concentration, are still not overall. Thus in this paper, we calculate the structural, electronic, and optical properties of different high concentration Sb−doped SnO₂, based on density functional theory (DFT) and analyze the results, which is expected to provide some theory evidence of doping modification about ATO.

2 Calulated methods and theoretical descriptions

2.1 Calculated methods

The theoretical calculations are processed by plane wave pseudo potential method based on the density functional theory\(^{[13]}\). The pseudo−potentials are used to replace ionic potentials, and the electronic wave function is expanded by plane wave basis sets. The electron−electron exchange and associate potential are corrected by the local density approximation (LDA), which is an accurate theory method of electronic structure calculation\(^{[14]}\). The electronic, optical properties of intrinsic and Sb−doped SnO₂ super cell are calculated through the vienna ab−initio simulation package (VASP) program\(^{[15]}\). As shown in Fig.1, the SnO₂ 2×2×2 super cell contain 16 Sn atoms and 32 O atoms and the number of Sb to replace Sn is 1−3, whose doping concentration is \(x = 6.25\%\), \(x = 12.5\%\) and \(x = 18.75\%\) correspondingly. In the calculation, the experimental lattice constant of SnO₂ is taken, that is, \(a = b = 0.4737\) nm, \(c = 0.3186\) nm, \(\alpha = \beta = \gamma = 90^\circ\). The energy cut−off of plane wave takes 380 eV, while Monkhorst − Pack mesh of Brillouin−Zone sampling takes 6×6×4, and the self−consistent convergence of the total energy takes \(5\times10^{-7}\) eV/atom for intrinsic and Sb−doped SnO₂ super cells. The atomic configuration for O, Sn and Sb are \(2s^22p^4\), \(5s^25p^5\), and \(5s^25p^3\), respectively. For intrinsic SnO₂, the net charge between Sn atom and Sn atom is all 0.58 e, and the net charge between O atom and Sn O is all −0.29 e, which means that same atoms are equivalent.

Fig.1 SnO₂, 2×2×2 super cell (black ball is Sn atom, grey ball is O atom, the Sn of position 1−3 is substituted for Sb)

2.2 Theoretical descriptions

The complex dielectric function \(\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)\), which can reflect band structure and other spectrum information, is usually used to describe the optical properties of solidity macroscopically. Where \(\varepsilon_r = n^2 - k^2\), \(\varepsilon_i = 2nk\) and \(n\) is the reflection coefficient, \(k\) stands for the extinction coefficient\(^{[17]}\). The real part can be obtained by Kramer–Kroing dispersion relation and imaginary part can be obtained by momentum matrix elements of wave function between occupied states and unoccupied states\(^{[18-19]}\).
The derivation process is ignored, and only giving the results.

\[ \varepsilon_1(\omega) = 1 + \frac{8\pi^2 e^2}{m^*} \sum_{\mathbf{k} \in BZ} \frac{2}{2\pi} \left| e_{MCV}(\mathbf{k}) \right|^2 \times \frac{\hbar^2}{\left[ E_c(\mathbf{k}) - E_v(\mathbf{k}) \right]^2 - \hbar^2 \omega^2}, \]  

\[ \varepsilon_2(\omega) = \frac{4\pi^2}{m^* \omega} \sum_{\mathbf{k} \in BZ} \left| e_{MCV}(\mathbf{k}) \right|^2 \times \delta \left[ E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar \omega \right], \]  

\[ I(\omega) = \sqrt{2}(\omega) \left[ \varepsilon_1(\omega)^2 - \varepsilon_2(\omega)^2 - \varepsilon_1(\omega) \right]^{1/2}, \]  

\[ R(\omega) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \]

Where \( C, V \) is conduction band and valence band, \( BZ \) is first Brillouin-zone, \( \omega \) is light frequency, \( K \) is reciprocal vector, \( \left| e_{MCV}(\mathbf{k}) \right|^2 \) is momentum transition matrix element. The above equations are the theory evidences of analyzing crystal band structure and optical properties. It reflects the luminescence mechanism generated by the electronic transitions between the energy levels.

3 Results and discussion

3.1 Electronic properties

As mentioned in paper\(^{[20]}\), when the order of magnitude of doping concentration is lower than \( 10^{18} \text{ cm}^{-3} \), the situation is considered as low doping, and that regards as high doping when the order of magnitude is equal or greater than \( 10^{19} \text{ cm}^{-3} \). The Sb-doped SnO\(_2\) are all high doping, and the result of Fermi level goes into the conduction band in the latter analysis further proved that.

The energy band structures of intrinsic SnO\(_2\) and Sb-doped SnO\(_2\) are shown in Fig.2.

![Fig.2 Calculated band structure of Sb-doping SnO\(_2\). (a) x=0%; (b) x=6.25%; (c) x=12.5%; (d) x=18.75%](image)

From the Fig.2, it can be seen that the Sb-doped SnO\(_2\) is direct band-gap semiconductor like intrinsic SnO\(_2\). The Fermi level is chosen to be zero of the energy scale, and the occupied state below the Fermi energy is valence band, whereas the unoccupied state lying above the Fermi energy is conduction band. The position of bottom of conduction band and top of valence band is G-point of Brillouin zone. The band gap are \( 1.285 \text{ eV}, 1.047 \text{ eV}, 0.791 \text{ eV}, 0.570 \text{ eV} \) for \( x=0\% \), \( x=6.25\% \), \( x=12.5\% \) and \( x=18.75\% \) Sb doping concentration of SnO\(_2\), respectively, which are all lower than available experimental data \( (3.7\sim3.8 \text{ eV}) \) mentioned in this paper\(^{[9]}\). This is because LDA is ground state theory, and the energy-gap belongs to property of excited state\(^{[21]}\). The calculated band gap of intrinsic SnO\(_2\) is closed to the calculated result 1.3 eV of paper\(^{[5]}\), which
proves that the method and adopted process are right. In order to make the band gap approach the experimental data, the scissors are set to 2.4 eV in the later optical properties calculation.

The band gap of Sb-doped SnO$_2$ is reduced in succession with the increase of Sb doping concentration, and the Fermi energy level moves into the conduction band. Compared intrinsic SnO$_2$, the amount of energy level of Sb-doped SnO$_2$ obviously increase, especially in the valence band, which means that the number of transition electrons between energy level increase. Therefore, the conductivity of Sb-doped SnO$_2$ improves. The energy level of conduction band is winding and overlap with the increase of Sb doping concentration, because there are great number of surplus electrons at the bottom of conduction band when the Fermi level goes into the conduction band. According to the theoretical analysis of renormalization, that is mainly because the high Sb doping concentration makes free charges changed the band gap of SnO$_2$ in two aspects. In one hand, high Sb doping concentration brings Burstein–Moss movement, and the edge of optical absorption moves to low energy direction, which lead to widening band gap. On the other hand, the interactions among charges makes multi-body effect or overlapping between impurity band and defect band, which makes the band gap narrow. The two aspects compete with each other, and with the increase of Sb doping concentration, Burstein–Moss effect is less than multi-body effect, so for high Sb doping SnO$_2$, the more concentration the narrower band gap.

The total density of state (TDOS) and partial density of states (PDOS) of intrinsic SnO$_2$ and Sb-doped SnO$_2$ are shown in Fig.3.

Fig.3 Calculated TDOS and PDOS for x=0%, x=6.25%, x=12.5% and x=18.75% Sb doping concentration of SnO$_2$: (a) TDOS; (b) Sn 5s, Sn 5p PDOS; (c) O 2s, O 2p PDOS; (d) Sb 5s, Sb 5p PDOS

From the Fig.3, it is found that TDOS of Sb-doped SnO$_2$ has a red shift with the decrease of band gap and the positions of peak values are mainly identical. From the Figure of density of state of 6.25% Sb-doped SnO$_2$, we can find that the valence band includes two parts, the low valence band, -22.5~13.0 eV region, which is dominated by O 2s$^2$ states, with a minor presence of Sn 5s$^2$, Sn 5p$^2$, Sb 5s$^2$ and Sb 5p$^3$ states, which can be ignored because it is far from Fermi level that has little influence with it. The high valence band can be divided into two sections, -13.0~9.5 eV region is dominated by Sn 5s$^2$ and Sb 5s$^2$ states, which raise with the increase of Sb doping concentration, and -9.5~0 eV region, which is closed to Fermi level, is dominated by O 2p$^4$ and Sn 5p$^3$ states, with a few contributions of Sb 5p$^3$ states which still enhance with the increase of Sb doping concentration. It illustrates that O atom can absorb electrons strongly from Sb atom and Sn atom. The conduction band is mainly dominated by Sn 5p$^2$, Sn 5s$^2$, Sb 5s$^2$ and Sb 5p$^3$, and O 2p$^4$ have a few
contributions. Combined the TDOS, PDOS and the energy band structure, there is a about 1 eV width band at the 12 eV point, which is mainly caused by Sb 5s², and with the increase of Sb doping concentration, the width broaden.

Figure.3 (a) shows that the TDOS of Sb–doped SnO₂ at Fermi level is affected by Sb doping, and the influence strengthens with the increase of Sb doping concentration, which also influences the optoelectronic properties of SnO₂ materials. The electrons at Fermi level distribute asymmetrically and Sb– doped SnO₂ materials present half–metallic property, which mainly due to Sb 5s² states and is corresponding to the increasing number of energy levels at Fermi level towards Brillouin zone in the energy band structure Figure. Meanwhile, the total density of state shift towards low energy direction with the increase of Sb doping concentration, which mainly lead to Fermi level going into conduction band and making the band gap narrower.

For intrinsic SnO₂, from Fig.3 (b),(c), it is found that Sn–5s and O–2p orbital electrons interact to form anti–bonding–like state of s orbital and bonding state of p orbital, which produce band gap. For Sb–doping SnO₂, as shown in Fig.3 (b)–(d), at the bottom of conduction band, Sb–5p orbital electrons has lower energy than Sn–5s, and Sb–5p and O–2p orbital electrons form anti–bonding–like state of p orbital, which has lower energy than anti–bonding–like state of s orbital in intrinsic SnO₂. Sb–5p orbital moves to low energy that leads to the descending of conduction band. With the increase of Sb high doping concentration, the movement towards low energy and the conduction band descending are all more obvious. In addition, the p–p orbital interaction makes valence band moving to low energy, and p–d repelling effect causes valence band moving to high energy. From the calculated results, it can be seen that with the increase of Sb high doping concentration, p–p interaction is stronger than p–d repelling effect, and the valence band descends more. However, with the increase of Sb high doping concentration, the conduction band is descending more than valence band, so the band gap is narrower.

3.2 Charge density

The charge density in the (1 1 1) basal plane for of intrinsic SnO₂ and Sb–doped SnO₂ are shown in Fig.4.

![Fig.4 Calculated total charge density of different Sb–doping concentration SnO₂.](image)

(a) x=0%; (b) x=6.25%; (c) x=12.5%; (d) x=18.75

Figure 4 shows that there are great atomic bonding properties differences between intrinsic SnO₂ and Sb– doped SnO₂, and the charge is redistributed. For intrinsic SnO₂, Sn atoms and O atoms form covalent bond, which contain ionic bond. However, for Sb–doped SnO₂, the charge distribution of atoms around doped Sb is effected and the electron communization improves. With the increase of Sb doping concentration, the ionicity enhances. Sb atoms and O atoms around it form overlapping regions of charge density, and the overlapping strengthens with the Sb–doping concentration increased. As a whole, electrons gather from Sb atoms to O atoms.
3.3 Optical property

The experimental result of Ref. [10] shows that Sb−doped SnO₂ has (1 1 0) preferred orientation, so the complex dielectric functions of intrinsic SnO₂ and Sb-doped SnO₂ from the polarization vectors (1 1 0) are calculated, and they are shown in Fig. 5.

![Fig. 5 Calculated complex dielectric function of different Sb-doping concentration SnO₂.](image)

(a) \( x = 0 \% \); (b) \( x = 6.25 \% \); (c) \( x = 12.5 \% \); (d) \( x = 18.75 \% \)

From the Fig. 5, we can see that the real part \( \varepsilon_1(\omega) \) is descended as a whole as the energy increases, and the intensity reaches maximum at 4.28 eV, 2.75 eV, 2.83 eV, 2.65 eV for \( x = 0 \% \), \( x = 6.25 \% \), \( x = 12.5 \% \) and \( x = 18.75 \% \) Sb doping concentration of SnO₂. The probability of photon absorption is directly related to the imaginary part of complex dielectric function \( \varepsilon_2(\omega) \). For \( \varepsilon_2(\omega) \), the points of curves beginning to rise are very consistent with the calculated energy gaps which add scissors, and there are three main transition peaks at the low energy region. The peaks appear because of the electrons transition from valence band to conduction band. The position of first peak is wide, which is about 3.39~5.08 eV, and the peak value increases with the increase of Sb doping concentration. The first peak arises from O 2p\(^{\prime}\) orbits to Sn 5s\(^i\) orbits, and some arise from Sb 5s\(^i\) orbits to Sn 5s\(^i\) orbits for Sb-doped SnO₂. The second peak is at about 6.50 eV, which mainly results from O 2p\(^{\prime}\) orbits to Sn 5p\(^i\) orbits, and some arise from Sb 5s\(^i\) orbits to Sn 5p\(^i\) orbits for Sb-doped SnO₂. The third peak, whose position is at about 9.56 eV, appears because of O 2s\(^i\) orbits to Sn 5s\(^i\) orbits, and some arise from Sb 5p\(^3\) state and O 2p\(^4\) state have strong coupling and lead to the changing of impurity level in the band gap. With the increase of Sb doping concentration, the transition peaks have a red shift towards low energy direction as a whole, and that is in accord with the previous calculated band gap, which is reduced with the Sb−doping concentration increased.

4 Conclusion

In conclusion, the electronic structures and optical properties of Sb−doped SnO₂ by plane−wave pseudopotential DFT with LDA are studied. The band gap for \( x = 0 \% \), \( x = 6.25 \% \), \( x = 12.5 \% \) and \( x = 18.75 \% \) Sb doping concentration of SnO₂ is narrower in succession and the Fermi level moves into conduction band gradually. According to the theoretical analysis of renormalization and orbital theory, the reason of above calculated results is analyzed. With the increase of Sb doping concentration, the transition peaks have a red shift towards low energy direction as a whole, and that is in accord with the previous calculated band gap, which is reduced with the Sb−doping concentration increased.

References


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