Impact of boron and indium doping on the structural, electronic and optical properties of SnO₂

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Research Article

Keywords: tin dioxide (SnO₂), optoelectronic devices

Posted Date: April 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-393104/v1>

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Abstract

Tin dioxide (SnO_2), due to its non-toxicity, high stability and electron transport capability represents one of the most utilized transition metal oxides in many optoelectronic devices such as photocatalytic devices, photovoltaics (PVs) and light-emitting diodes (LEDs). However, its wide bandgap reduces its charge carrier mobility and its photocatalytic activity. Doping with various elements is an efficient and low-cost way to decrease SnO_2 band gap and maximize photocatalytic applications' potential. Here, we apply density functional theory calculations to examine the effect of p-type doping with B and In of SnO_2 on its electronic and optical properties. Calculation predict the creation of shallow energy states in the band gap, near the valence band, when the dopant (B or In) is in interstitial position. In the case of substitutional doping, a significant decrease of the band gap is calculated. We also investigate the effect of doping on the surface sites of SnO_2 . We find that B incorporation in the (110) does not alter the gap while In causes a notable decrease. The present work highlights the significance of boron and indium doping in SnO_2 both for solar cells and photocatalytic applications.

Introduction

Tetragonal SnO_2 is a wide bandgap semiconductor which typically shows n-type conductivity due to the oxygen vacancies that are created during the crystallization process ^[1–4]. SnO_2 is commonly used for glazes ^[1], polishing powder ^[2], photovoltaics^[3], and gas sensors ^[4]. Recently, SnO_2 has been demonstrated as a cathode material in Li-ion batteries ^[5]. Wang et al. ^[5] have shown that Sn_2O_3 in SnO_2 nanosheets significantly improves battery performance. However, the common SnO_2 films exhibit low intrinsic carrier mobility, which has been attributed to deep donor states originating from oxygen vacancies^[3]. Many doping strategies have been adopted to further increase its electrical conductivity and improve its absorption in the visible region –for photocatalytic applications- by reducing its wide energy gap. Specifically, many experimental and theoretical works have demonstrated that halogen doping in SnO_2 increases conductivity and transparency, making it a better candidate for optoelectronic applications ^[6, 7].

Another option for improving the properties the properties of SnO_2 is doping with p-type elements ^[8]. Transparent conducting oxides (TCOs) fabricated from doped semiconductor oxides such as In: SnO_2 (ITO), F: SnO_2 (FTO) and B: ZnO (BZO) are commonly used as transparent conductive materials in industrial applications such as displays and lighting devices ^[8]. In these structures, the metal atom is generally substituted by the dopant, which improves the charge carrier conductivity. Experimental reports on mesoporous oxides indicate remarkable chemical properties when boron in an interstitial position ^[9]. These boron interstitials enhance the carrier densities of the semiconductors and help to adopt a diverse coordination environment with abundant oxygen vacancies. Additionally, some reports propose boron as a doping candidate for SnO_2 based photocatalytic applications ^[10].

Apart from the experimental works, there are also many theoretical studies based on density functional theory (DFT) that examine the influence of doping in SnO_2 , mostly in substitutional positions ^[11–17]. Especially for the halogen substitutional doping, it is revealed that single donor states arise inside the bandgap; however, the effect of interstitials is not generally taken into consideration by the community.

In most previous DFT studies, tin oxide bandgap is underestimated and predicted at a value of 1–2 eV ^[17–18]. This is a well-known deficiency of the Local Density Approximation (LDA) and of the Generalized Gradient Approximation (GGA). Therefore, the use of computationally demanding but more accurate hybrid exchange-correlation functionals are deemed necessary to accurately describe the band gap and the position of states in the gap or at its edges.

In the present study, we apply Hybrid functional DFT calculations using PBE0 ^[45] achieve a bandgap value of 3.35 eV, which agrees well with the experimentally reported prediction ^[3, 19]. More analytically, we examine the effect of boron and indium doping on the bulk SnO_2 and we also investigate the effect of interstitial doping of the (110) surface for the first time. Density of states (DOS) calculations showed a reduction of the band gap in all cases, which is more profound for the interstitial doping and formation of energy states in the bandgap for the substitutional doping. This bandgap reduction combined with the created intergap energy levels are highly beneficial for the photocatalytic applications of SnO_2 while the predicted characteristics can also be applied in photovoltaic technologies.

Results

Bulk rutile SnO_2

SnO_2 forms in the $P4_2/mmm$ space group and crystalizes in a rutile structure. The experimental unit cell parameters $a = b = 4.737 \text{ \AA}$ and $c = 3.186 \text{ \AA}$ were determined using X-ray diffraction (XRD) experiments ^[11]. The calculated lattice parameters after the relaxation of rutile SnO_2 are $a = b = 4.717 \text{ \AA}$ and $c = 3.189 \text{ \AA}$ in good agreement with the experimental values. The dopant percentage of our calculations is 1 B or In atom per 48 SnO_2 atoms, which results in a 2.08% additional doping. Zhang *et al.* ^[20] performed experiments regarding the effect of boron in tin oxide and they predicted that boron can either substitute a tin atom or occupy an interstitial position. We predict that for the substitutional case, boron atom occupies a tin site and is located at a distance of $1.775 \text{ \AA}$ from the nearest oxygen atom (refer to Fig. 1a) while for the interstitial case, the boron atom sites at a distance of $1.475 \text{ \AA}$ from the O-atom (refer to Fig. 1b). In Figs. 1c and 1d we show the $\text{In}_{\text{Sn}}:\text{SnO}_2$ and $\text{In}_i:\text{SnO}_2$ cases, respectively. The substitutional dopant is relaxed at a distance of $2.11 \text{ \AA}$ from the nearest oxygen atom, while the interstitial is located at a distance of $2.03 \text{ \AA}$. In Table 1, we report the relevant lattice parameters and volume changes, through doping, for the bulk system. Concerning the $\text{B}:\text{SnO}_2$ cases, there is a small decrease in the lattice volume for the substitutional case, which can be attributed to the smaller ionic radius of B than Sn ($\text{B}^{3+}:0.23 \text{ \AA}$, $\text{Sn}^{4+}:0.71 \text{ \AA}$) while for the interstitial case, there is an increase. The present results agree with the available experimental data that predict a decrease of the lattice parameters for the $\text{B}_{\text{Sn}}:\text{SnO}_2$ and an

increase for the $B_i:\text{SnO}_2$ [9]. Similarly for the $\text{In}:\text{SnO}_2$ we predicted that in all the cases, there is an increase to the lattice parameters. This agrees with previous experimental studies [21].

Table 1
The calculated lattice constants and cell volumes for all the dopants.

	$a(\text{\AA})$	$c(\text{\AA})$	Vol ($\text{\AA}^3$)
SnO_2	4.717	3.189	70.956
$B_{\text{Sn}}:\text{SnO}_2$	4.674	3.153	68.881
$B_i:\text{SnO}_2$	4.866	3.225	76.361
$\text{In}_{\text{Sn}}:\text{SnO}_2$	4.730	3.194	71.459
$\text{In}_i:\text{SnO}_2$	4.901	3.220	77.343

For each doping case, we calculate the DOS and the PDOS and present them in Fig. 2. The DOS of the undoped SnO_2 is illustrated in Fig. 2e for reference. To have a clear and more reliable picture of the changes of the electronic structure due to doping, we use for our calculations the hybrid functional PBE0, which provides a good bandgap value for our model (calculated at 3.35eV) and in agreement with previous theoretical works [7] and the experimental value [19].

In Fig. 2a, the $B_{\text{Sn}}:\text{SnO}_2$ case is examined. In this case, it is observed from the total DOS (grey) that the bandgap is reduced to the value of 3eV while some energy states are created inside the bandgap at 1eV. Furthermore, it is seen that some additional states arise at the valence band maximum. Looking at the PDOS of the boron substitutional case, we predict that these states are created mostly from the hybridization of O-2p with Sn-5p and the B-2p orbitals. Our prediction agrees well with the work of Yu *et al.* [22], which also predicts mid-gap states and gap reduction when boron is inserted. However, in their study, there is an underestimation to the bandgap value of tin dioxide. Similar experimental studies [23] have shown that 2% boron doping reduces the bandgap 0.4 eV, which is identical to the reduction we predicted.

To further investigate the effect of boron doping, we investigate the effect of interstitial boron in tin oxide. We expect that the interstitial incorporation of boron results in gap states forming to the conduction band edge. The bandgap is seen to increase to the value of 3.9 eV. As it is discussed in previous works, the formation of energy states in the middle of the gap is highly beneficial for photocatalytic applications, but still, they can be a crucial disadvantage for PV and LED devices as they work as “traps” which reduce the device photocurrent and the photogenerated charge carriers [24, 25]. Although $B_i:\text{SnO}_2$ has not been examined theoretically yet, Zhi *et al.* [9] predicted that interstitial atomic positions play a significant role in

increasing the capacity of tin oxide, making it a good fit for supercapacitor applications. In fact, in their work, they used a 4% doping percentage of boron and they concluded that the interstitial atoms slightly increased the bandgap. This phenomenon is called the “Moss-Burstein effect” and it is generally seen in heavily doped semiconductors, where after a doping concentration, the bandgap of the semiconductor starts to increase even reaches higher values than the undoped material ^[26]. In the case of $B_i : \text{SnO}_2$, this provides a sufficient number of charge carriers that improve the capacitance of SnO_2 ^[27]. We predicted this bandgap increase both in the case of the bulk SnO_2 and in the (110) surface of SnO_2 . The (110) plane is considered the most highly energetic plane of the experimental SnO_2 structure ^[9, 28, 29] as we discuss in the next section and our calculations complete the DFT work of Zhi *et al.* ^[9] which gave emphasis only to the (002) plane.

Continuing with the bulk $\text{In}:\text{SnO}_2$ we examined the interstitial and substitutional formation again. Focusing on the DOS of $\text{In}_{\text{Sn}} : \text{SnO}_2$ (Fig. 2c) we predicted again unoccupied energy states near the valence band at 0.8eV, which are created due to the hybridization of O-2p with Sn-5p and In-5p. These gap states might be beneficial for device fabrication as they will serve as a route for the transition from the valence to the conduction band. Furthermore, it is seen that this time the bandgap is slightly decreased at a value of 3.25eV. Lastly, we performed calculations for the interstitial doping of indium in tin oxide. We predict that the In-5p orbitals play a significant role in shifting the conduction band and reducing the band gap, which reaches a value of 1.9 eV. Like the boron case, the interstitial doping does not give rise to any energy levels inside the gap. The present results agree well with the experimental data of Abdulsattar *et al.* ^[30], which predicted a slight decrease to the bandgap with a doping percentage of 2%. All these results show that although $B:\text{SnO}_2$ shows energy states that are detrimental for device applications, its evident gap reduction makes it possible for photocatalytic applications. In contrast, $\text{In}:\text{SnO}_2$ shows characteristics that make it a good candidate for electron transport layer material for photovoltaic devices.

To consider possible applications of the doped structures, we calculated all the bulk doped cases' optical properties. Firstly, to describe the absorption and dispersion mechanisms from the occupied to the empty electron levels, we predicted the dielectric function, presented in Fig. 3. Focusing on the real part of the dielectric function for the undoped SnO_2 (dotted purple), it is seen that it reaches a maximum value of 8.5eV. The negative value at 16.5eV is attributed to the metallic properties of undoped SnO_2 ^[31–32]. The imaginary part of the dielectric function provides us helpful information regarding the probability of photon absorption. We calculated that there is a decreasing trend for all the cases due to the Maxwell-Wagner interfacial polarization ^[33]. From the undoped SnO_2 case (dotted green), two sharp peaks arise due to the transitions from O-2p to Sn-5p. The dielectric constant of the undoped case is predicted at 2 in good agreement with previous experimental ^[31] and theoretical works ^[32]. Focusing on $B_{\text{Sn}} : \text{SnO}_2$ (refer to Fig. 3a) case, we predicted the dielectric constant is significantly increased to the value 2.5. The major peak that arises at 1.7eV of the imaginary part can be attributed to the transition of electrons of B-2p and

the Sn-5p. Continuing with the interstitial B case (refer to Fig. 3b), there is an evident increase to the dielectric constant, which reaches a value of 3.8.

Regarding the $\text{In}_{\text{Sn}}:\text{SnO}_2$ (Fig. 3c) the dielectric constant is increased to the value of 3, which is significantly higher than the $\text{B}_{\text{Sn}}:\text{SnO}_2$ and finally, for the $\text{In}_{\text{i}}:\text{SnO}_2$ (Fig. 3d) the dielectric constant reaches the value of 3.7. From Fig. 3 it can also be seen that there is a shift of the low photon energy peaks towards the visible region accompanied by an increase of the value of the dielectric constant. The recombination of charge carriers decreases in this kind of material, where the static dielectric constant monitors the electric fields inside the material by polarization. As a result, both the $\text{B}_{\text{i}}:\text{SnO}_2$ and $\text{In}_{\text{i}}:\text{SnO}_2$ are highly preferred to use as heterojunction buffer layers in photovoltaic applications.

The refractive index is shown in Fig. 4. For the SnO_2 the refractive index is computed in zero frequency at the value of 1.40, which agrees with other simulation works ^[32], but it is underestimated compared to the experimental value of 1.70 ^[34].

Regarding the doping structures, we predicted a value of 1.55 for the $\text{B}_{\text{Sn}}:\text{SnO}_2$ (Fig. 4a), while for the $\text{B}_{\text{i}}:\text{SnO}_2$ (Fig. 4b), there is an increase reaching a value of 1.95. Looking at the indium doping cases, we predicted a value of 1.6 for the substitutional case (Fig. 4c) and a value of 1.85 for the interstitial dopant (Fig. 4d). It is evident that for the refractive index, there is an increase in the lower photon energies and on contrary, there is a significant decrease in the upper energies. This is due to the optical dispersion that these structures have.

To provide a further insight into the optical properties of all these structures, in Fig. 5 we calculated the reflectivity, the optical conductivity, and the absorption of the structures. Reflectivity (see Fig. 5a) is one of the most important properties of these materials because it signifies the amount of photons that are reflected from the material. We have shown that the values at zero photon energy are calculated at 3%, 5%, 10%, 6% and 9.5% for SnO_2 , $\text{B}_{\text{Sn}}:\text{SnO}_2$, $\text{B}_{\text{i}}:\text{SnO}_2$, $\text{In}_{\text{Sn}}:\text{SnO}_2$ and $\text{In}_{\text{i}}:\text{SnO}_2$ respectively. We predicted that $\text{B}:\text{SnO}_2$ has the highest reflectivity in the near-infrared and visible regions compared to all the other cases. It can also be seen that all the examined cases encounter less than 15% reflectivity in the infrared and visible region; thus they can be used as antireflective coatings when the dopant concentration is at 2% ^[35]. In Table 2 we have gathered all the calculated electrical and optical constants for reference.

Table 2
The calculated electronic and optical constants for all the examined cases.

	Bandgap (eV)	Dielectric constant	Refractive index	Reflectivity
SnO ₂	3.33	2.0	1.40	0.03
B _{Sn} :SnO ₂	3.00	2.5	1.55	0.05
B _i :SnO ₂	3.90	3.8	1.95	0.1
In _{Sn} :SnO ₂	3.25	3	1.60	0.06
In _i :SnO ₂	3.75	3.7	1.85	0.095

In Fig. 5b we present the optical conductivity of all the calculated structures. If a photon has higher energy than the optical bandgap then a transition occurs and an electron-hole pair (exciton) is generated. The mobility of these excitons represent the optical conductivity, which is an important parameter that is used to design optical detectors [36]. Because of the electronic charge neutrality, these excitons do not contribute to the electrical conductivity [37]. The highest excitonic features are calculated at 13.2eV for undoped, B_{Sn}:SnO₂ and In_{Sn}:SnO₂ cases while for the interstitial dopants they are shifted to 9eV and 10eV for the B and In, respectively. The optical conductivity also describes the losses for a wave with the same frequency. From the graph, we can conclude that SnO₂ and In_i:SnO₂ have lower losses than the other cases. Lastly, in Fig. 5c and 5d we present the absorption co-efficiency. The undoped case's absorption starts at 380nm, which is underestimated compared to the experimental value, which is approximately 400nm [38]. It is seen that In_i and B_i have the highest absorption to the visible region.

From the above, we can conclude that both B_i and In_i exhibit interesting characteristics, making them applicable to photovoltaic and photocatalytic devices.

Surface (110) of rutile SnO₂

As Zhi *et al.* [9] indicated in their work, to further understand the effect of boron interstitial, the surface of SnO₂ should be examined. For applicable photocatalytic materials with a visible light response and high charge mobility, such as tin dioxide, attention to the high-energy surfaces should be paid when the structure is doped with atoms or molecules. However, it is seen that the studies of SnO₂ surface are significantly less than the studies of the bulk and they primarily focus on sensor applications of tin oxide [39]. In this section, the change to the electronic properties of B and In doped SnO₂ will be investigated and discussed. Here we used a slab model with a vacuum of 12 Å thickness across the (110) plane. We chose this particular surface because it is the most intense crystallization plane [9, 39] of the rutile SnO₂ and it has never been studied before regarding the B or In doping. Furthermore, as the (110) plane is one of the

most highly energetic surfaces, it will play the role of the active site in photocatalytic reactions^[40]. For our DOS and pDOS calculations we used hybrid calculations again.

In Figs. 6a-6b we present the B_i :SnO₂ and In_i :SnO₂ doping cases. It is seen that the boron interstitial displaces the tin atom and occupies a tin site to minimize its energy (Fig. 6a). We predicted that interstitial boron sites at 2.182 Å from the nearest oxygen atom and 3.10 Å from the nearest tin atom. On the other hand, we calculated that indium atom sites at a distance of 2.183 Å from the nearest oxygen atom and 3.32 Å from the nearest tin atom. Looking at the DOS and the pDOS of Fig. 7a, it is seen that boron interstitial produces a small band peak at 1eV.

Interestingly in this high-energy plane the bandgap isn't decreased compared to the undoped (see Fig. 7c). We believe that this result combined with the bulk B_i :SnO₂ explains the experimental phenomenon that Zhi et al [9] discussed in their paper about B_i . Looking at the In_i :SnO₂ (refer to Fig. 7b) we can see that the (110) surface bandgap decreases to 2eV. The gap of the undoped (110) SnO₂ is shown in Fig. 7c at 2.5eV, a good agreement with other DFT works^[41]. All the above results indicate that In doping in the SnO₂ shows good characteristics that should be examined in photocatalytic applications.

Conclusions

Herein, we applied DFT calculations for boron and indium rutile SnO₂ bulk and surface to evaluate the doping effect on the electronic and optical properties. Specifically, we performed DOS calculations and we found that the bulk structures have a bandgap increase and in the case of boron mid gap states are formed. Although these states might be detrimental for photovoltaics as they may act as trap states for photogenerated carriers, they can be the working horse for photocatalytic applications based on B:SnO₂. Our work explains some of the phenomena that have been experimentally observed and open the road for applications of boron structures to more applications such as supercapacitors. Regarding the indium defect, we predicted that at low concentrations highly wanted states are formed near the valence band which can be beneficial for energy harvesting devices. Furthermore, its optical characteristics and the bandgap reduction at the surface make it a worthy candidate for photocatalysis.

Methodology

All our results are based on the Cambridge Serial Total Energy Package (CASTEP)^[42–43]. For our calculations we used the hybrid functional PBE0 in order to consider the effect of the localized electrons and the bandgap underestimation that is generally encountered in GGA and LDA^[44]. The cutoff energy was chosen at 800eV after performing the convergence test and for our calculations we used an 48 atom supercell with 2x2x3 k-points for the sampling of the Brillouin zone during the geometry optimization^[44]. For the DOS calculations we used a k-point mesh of 5x5x5 for the bulk modelling while for the surface we applied a 3x3x1 set. Finally, the convergence criteria for our simulations were chosen at $2.0 \cdot 10^{-6}$

⁵eV/atom for the SCF tolerance, 0.05 eV/Å for the force tolerance and 0.001 Å for the Max displacement tolerance.

Declarations

Acknowledgements

P.P.F., M.V., D.D. and A.C. are grateful for LRF ICON funding from the Lloyd's Register Foundation, a charitable foundation helping to protect life and property by supporting engineering-related education, public engagement and the application of research. N.K. acknowledges support from European Union's H2020 Programme under Grant Agreement no 824072- HARVESTORE.

Contributions

P.P.F. and N.K. performed the calculations. P.P.F., N.K., M.V., D.D. and A.C. contributed to the interpretation of the results and the writing of the paper.

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Figures

Figure 1

The structures of (a) Boron substitutional doped SnO₂ (B Sn : SnO₂), (b) Boron interstitial doped SnO₂ (B i : SnO₂), (c) Indium substitutional doped SnO₂ (In Sn : SnO₂) and (d) Indium interstitial doped SnO₂ (In i : SnO₂).

Figure 2

The total density of states (DOS) and the projected density of states (PDOS) of (a) $\text{B}_{\text{Sn}}:\text{SnO}_2$, (b) $\text{B}_i:\text{SnO}_2$, (c) $\text{In}_{\text{Sn}}:\text{SnO}_2$, (d) $\text{In}_i:\text{SnO}_2$ and (e) undoped SnO_2 .

Figure 3

The dielectric function for (a) $\text{B}_{\text{Sn}}:\text{SnO}_2$, (b) $\text{B}_i:\text{SnO}_2$, (c) $\text{In}_{\text{Sn}}:\text{SnO}_2$ and (d) $\text{In}_i:\text{SnO}_2$. The dotted purple and dotted green, correspond to the dielectric function of the undoped SnO_2

Figure 4

The refractive index for (a) B Sn : SnO₂, (b) B i : SnO₂, (c) In Sn : SnO₂ and (d) In i : SnO₂. The dotted purple and dotted green, correspond to the dielectric function of the undoped SnO₂

Figure 5

(a) The reflectivity for all the doped structures (b) The optical conductivity for all the studied structures (c) the absorption coefficient for all the structures versus the photon energy (d) the absorption coefficient for all the structures versus the wavelength. The dotted purple and dotted green, correspond to the undoped SnO₂.

Figure 6

The structures of (a) Boron doped (110) SnO₂ surface and (b) Indium doped (110) SnO₂ surface.

Figure 7

The total density of states (DOS) and the projected density of states (PDOS) of (a) B (b) In and (c) Undoped (110) SnO_2 surface.