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# Study of Structural and Electronic properties of Non-metal Elements doped SnO<sub>2</sub>

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## Abstract

The crystal structure, electronic properties of F, S, C, B and N doped SnO<sub>2</sub> were studied with the First-Principle Method. The theoretical results show that doping of non-metal elements did not change the structure of SnO<sub>2</sub> but result in slight lattice volume expansion. The dope of the non-metal elements of B, F, and S cause the Fermi level to shift up. The most obvious finding to emerge from the analysis is that F-doped SnO<sub>2</sub> has the lowest defect binding energy, stable crystal structure, and the easiest doping. The B, F, and S element doped SnO<sub>2</sub> can modulate the fermi level. The doping of the B and S elements introduced additional defect energy levels to appear within the forbidden band-gap, which improved the crystal conductivity. Analysis of the energy band structure of SnO<sub>2</sub> crystals doped with C and N elements shows that the Fermi level has crossed the impurity level. The Fermi level of F doped SnO<sub>2</sub> is inside the conduction band, and the doped crystal has metallicity.

The optical properties of SnO<sub>2</sub> crystals doped with non-metallic elements were analyzed and calculated. The SnO<sub>2</sub> crystal doped with F element had the highest reflectivity in the infrared region, and the reflectance of the crystals doped with N, C, S, and B elements decreased sequentially. Based on this theoretical calculations, F doped SnO<sub>2</sub> is found to be the best photoelectric material for preparing low-e thin film.

Keywords: Doped SnO<sub>2</sub>, Electronic structure, DFT

## 1. Introduction

Thin-film solar cells are devices that convert solar energy into electrical energy. The transparent conductive films (TCF) is a thin film material that has both conductive capabilities and high transmittance in the visible light range (300 ~ 800nm)<sup>[1]-[3]</sup>. The TCFs serve as the front electrode of the thin-film solar cell. Up to now, the solar energy conversion efficiency is about 23.3%<sup>[4]</sup>, it is important to increase the photovoltaic power generation efficiency, as well as the performance of the front electrode.

The intrinsic SnO<sub>2</sub> semiconductor is not conductive due to the absence of free carriers. However, the band gap of 3.6eV of SnO<sub>2</sub> made it a potential ideal material for transparent electrode film. It had been proved that the doping of heteroatoms to replace Sn or O elements can lead to more carriers or holes, due to which, many research works have been done using different elements. Non-metallic atoms, such as fluorine, nitrogen etc. were proved to be proper elements for this purpose. After doping heteroatom, the preferred orientation, optical properties and electrical properties of SnO<sub>2</sub> films are improved.

Analysis of the electrical properties of SnO<sub>2</sub> thin films doped with different non-metallic elements showed that the resistance of SnO<sub>2</sub> thin films doped with N element was higher<sup>[5][6][7]</sup> than other doped SnO<sub>2</sub>.

Nguyen successfully prepared p-type N-doped SnO<sub>2</sub> film using magnetron sputtering technology [9]. The research results showed that the intrinsic SnO<sub>2</sub> thin film was an n-type semiconductor, and the concentration of free carrier in the thin film increased as the temperature for sedimentation increases. However, P-type semiconductors were successfully prepared with N-doped SnO<sub>2</sub> thin films. Through Al / N double doping, a p-type SnO<sub>2</sub> semiconductor thin film with excellent electrical properties was prepared. The resistivity, hole concentration and hole mobility of the thin film were  $7.1 \times 10^{-3} \Omega \text{ cm}$ ,  $6.24 \times 10^{19} \text{ cm}^{-3}$  and  $14.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [7]. Doping SnO<sub>2</sub> with F element (substituting element O) can effectively increase the carrier concentration and improve the conductivity of the film. R. Majumder successfully prepared SnO<sub>2</sub>: F thin film using spray pyrolysis method with SnF<sub>2</sub> as the precursor. By adjusting the concentration of the precursor solution, doped-SnO<sub>2</sub> films with different properties

were obtained. When the concentration of the precursor solution was adjusted to 0.15M and the substrate temperature was 773K, a film with a resistivity of  $1.2 \times 10^{-4} \Omega \cdot \text{cm}$  was prepared<sup>[8]</sup>.

Theoretically, based on the First-Principles, the doping of N to the SnO<sub>2</sub> crystal structure can introduce oxygen vacancies, and thus, increase the charge density of Sn sites. The replacement of O with N can simultaneously decrease the release of CO<sub>2</sub> gas.

There have been reports about the experimental research of non-metallic doped SnO<sub>2</sub>, but the mechanism of the effect of non-metallic element doping on SnO<sub>2</sub> performance is not clear enough. In this paper, the Density Functional Theory is used to analyze the electronic structure and optical properties of SnO<sub>2</sub> doped with non-metallic elements.

## 2. Crystal structure model and calculation method

The SnO<sub>2</sub> crystal has the tetragonal structure, its international space symmetry group symbol is P42 / MNM. There are 6 O<sup>-2</sup> ions in the nearest neighbor around each Sn<sup>4+</sup> site, and 3 Sn<sup>4+</sup> ions in the nearest neighbor around each O<sup>-2</sup> ion, so the coordination number for Sn and O are 6 and 3, respectively. The CASTEP package was used to construct a  $3 \times 2 \times 1$  tin dioxide supercellular structure system. In order to study the effect of doped non-metallic element on SnO<sub>2</sub> structure, N, C, B, F, or S was used to replace one O atom in the supercell, respectively. The model diagram of doped SnO<sub>2</sub> was shown in Figure 1. The red spheres were oxygen atoms, the gray spheres were tin atoms, and the light blue ones were non-metal atoms.

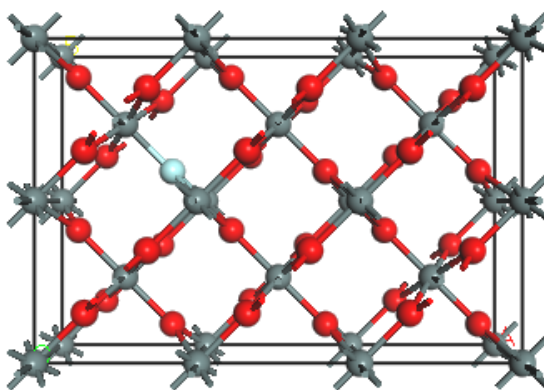


Fig.1 Schematic diagram of the structure of non-metal atom replacing O atom SnO<sub>2</sub> unit cell The red spheres were oxygen atoms, the gray spheres were tin atoms, and the light blue

ones were non-metal atoms.

The crystal structure optimization and electronic structure of the doped SnO<sub>2</sub> cell were obtained through the CASTEP program based on density functional theory. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) was selected as the exchange association functional. The interaction between inner electrons and valence electrons was described by OTFG ultra-soft pseudopotential.

The valence electronic configuration in the system are Sn 5s<sup>2</sup>5p<sup>2</sup>, O 2s<sup>2</sup>2p<sup>4</sup>, N 2s<sup>2</sup>2p<sup>3</sup>, C 2s<sup>2</sup>2p<sup>2</sup>, B 2s<sup>2</sup>2p<sup>1</sup>, F 2s<sup>2</sup>2p<sup>6</sup>, S 3s<sup>2</sup>3p<sup>4</sup>. The calculation parameters of the doping system were set as follows, the plane waves cut-off energy is 571.4eV, the B-Brillouin zone K space was divided by 2 × 3 × 8, the convergence accuracy of each atom was 10<sup>-5</sup>eV / atom, the internal stress between atoms was less than 0.05GPa, atoms displacement was less than 0.0001 nm.

### **3. Results and discussions**

#### **3.1 Structural optimization**

Table 1 shows the results of geometric optimization of the crystal structure of SnO<sub>2</sub> doped with non-metallic elements. After replacing O in SnO<sub>2</sub> with non-metallic elements (F, S, C, B, N), the crystal structure is distorted and the volume expands. Since the S atom is in the third period of the periodic table, its atomic radius is much larger than other doping atoms, the resulted volume expansion is 8.315%. According to the periodic table, the atomic radius of an element decreases from left to right, the lattice expansion rate also decreases in sequence. However, it can be noticed that the SnO<sub>2</sub> doped with F atoms has larger volume expansion. Therefore, it is necessary to analyze the bond formation before and after F atom doping, as shown in Table 3. It shows that Population value of Sn-F chemical bond is only 0.125, showing strong ionicity and strong ability to compete for electrons. The chemical bonds of other elements (C, B, N) and Sn elements exhibit the characteristics of covalent bonds. Therefore, SnO<sub>2</sub> doped with F element exhibits an abnormal lattice expansion rate.

Table 1 Geometric optimization results of O atom doping with nonmetallic substitutio

	Pure SnO <sub>2</sub>	SnO <sub>2</sub> :B	SnO <sub>2</sub> :C	SnO <sub>2</sub> :N	SnO <sub>2</sub> :F	SnO <sub>2</sub> :S
a (Å)	9.47454	9.74866	9.68215	9.66020	9.70223	9.74767
b (Å)	3.18638	3.24372	3.24956	3.24402	3.25942	3.25763
c (Å)	14.2118	14.6574	14.5507	14.4901	14.5451	14.6390
V (Å <sup>3</sup> )	429.048	463.456	457.802	454.088	459.934	464.725
ΔV%		8.02	6.702	5.836	7.1987	8.315

To evaluate the stability of the crystal structure of the doped lattice, it is necessary to calculate the defect binding energy of the lattice. It can be calculated according to equation below<sup>[9]</sup>.

$$E_{\text{bind}} = (E_{(\text{AB})} - E_{(\text{A})} - E_{(\text{B})}) / n$$

E (AB) is the total energy of the doped structure, E (A) and E (B) are the chemical potentials of atoms, and n is the total number of atoms in the unit cell structure. The total energy and binding energy of the doped structure are shown in Table 2.

Table2 Binding energy of substituting non-metallic atom for doped O atom

	Total Energy (eV)	Concentration (at%)	Binding Energy(eV)
SnO <sub>2</sub> :F	-3.55E+04	4.17	-5.38
SnO <sub>2</sub> :S	-3.52E+04	4.17	-5.24
SnO <sub>2</sub> :C	-3.50E+04	4.17	-5.27
SnO <sub>2</sub> :B	-3.49E+04	4.17	-5.22
SnO <sub>2</sub> :N	-3.51E+04	4.17	-5.33

Table 2 provides the defect binding energy of the doping system. The results are all negative, illustrates the doped crystal structures are all stable structures. The defect binding energy of each sample decreased in order of B, S, C, N, F. The SnO<sub>2</sub> doped

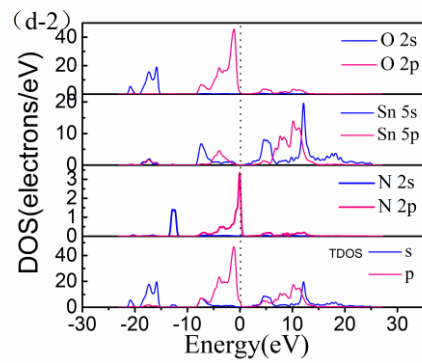
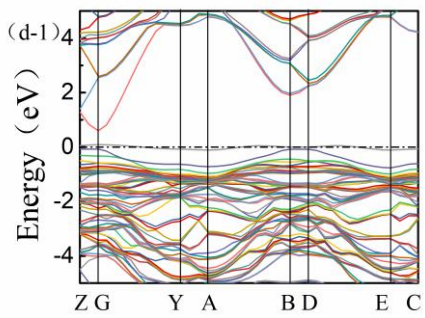
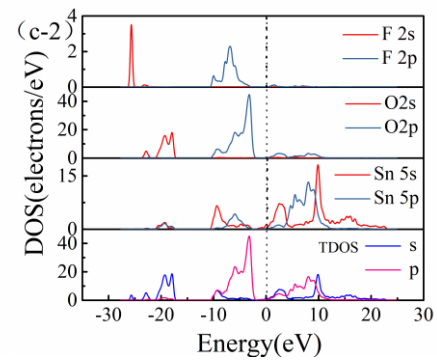
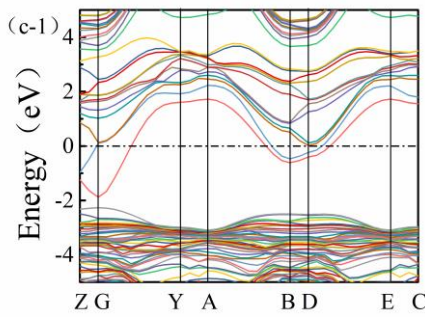
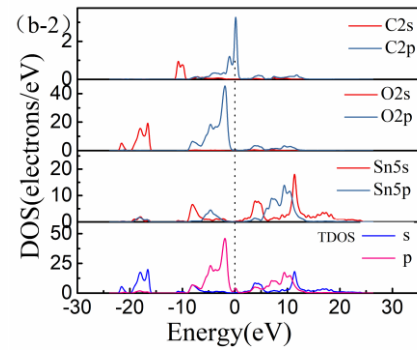
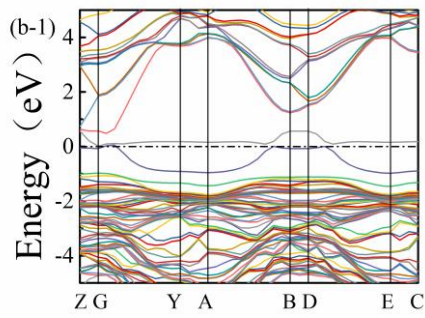
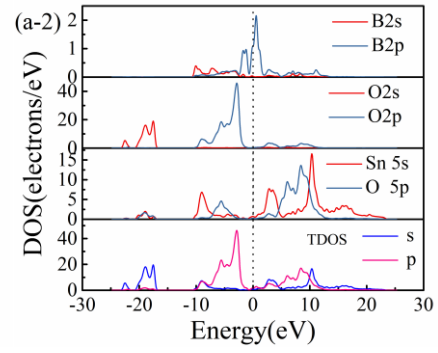
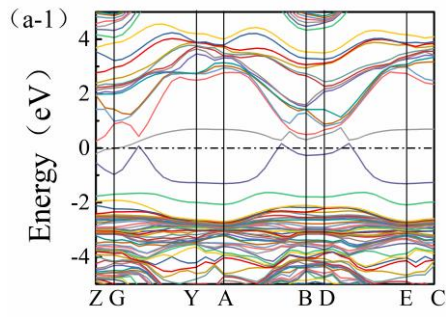
with F had the lowest binding energy which made it the most stable structure.

Table3 Bond length and charge of the crystal structure of non-metallic atom replacing doped O atom

	Average Bond Length ( $\text{\AA}$ )				Average net charge (e)		
	Sn-O	Population value	Sn-M	Population value	Sn	O	M
SnO <sub>2</sub>	2.054	0.505			2.07	-1.04	
SnO <sub>2</sub> :F	2.096	0.472	2.289	0.125	1.9	-0.967	-0.58
SnO <sub>2</sub> :S	2.099	0.499	2.427	0.705	1.907	-0.966	-0.67
SnO <sub>2</sub> :C	2.095	0.5	2.186	0.885	1.918	-0.967	-0.75
SnO <sub>2</sub> :B	2.099	0.484	2.324	0.905	1.895	-0.964	-0.56
SnO <sub>2</sub> :N	2.091	0.496	2.105	0.695	1.964	-0.967	-0.95

### 3.2 Band structure and density of states

Due to the addition of non-metallic atoms, not only the crystal structure was distorted, but also the electronic structure of the SnO<sub>2</sub> crystal is changed. The doping atoms introduce impurity levels in the band gap of SnO<sub>2</sub>, which changes the electronic structure of the system. The different properties of each doping atom make SnO<sub>2</sub> electronic structure different changes. The SnO<sub>2</sub> crystal shows metallicity when the introduction of non-metallic atoms causes the Fermi level to enter the conduction band. The electronic structure Including the energy band structure, total state density and partial wave state density of the non-metallic element doping system are shown in Figure 2.





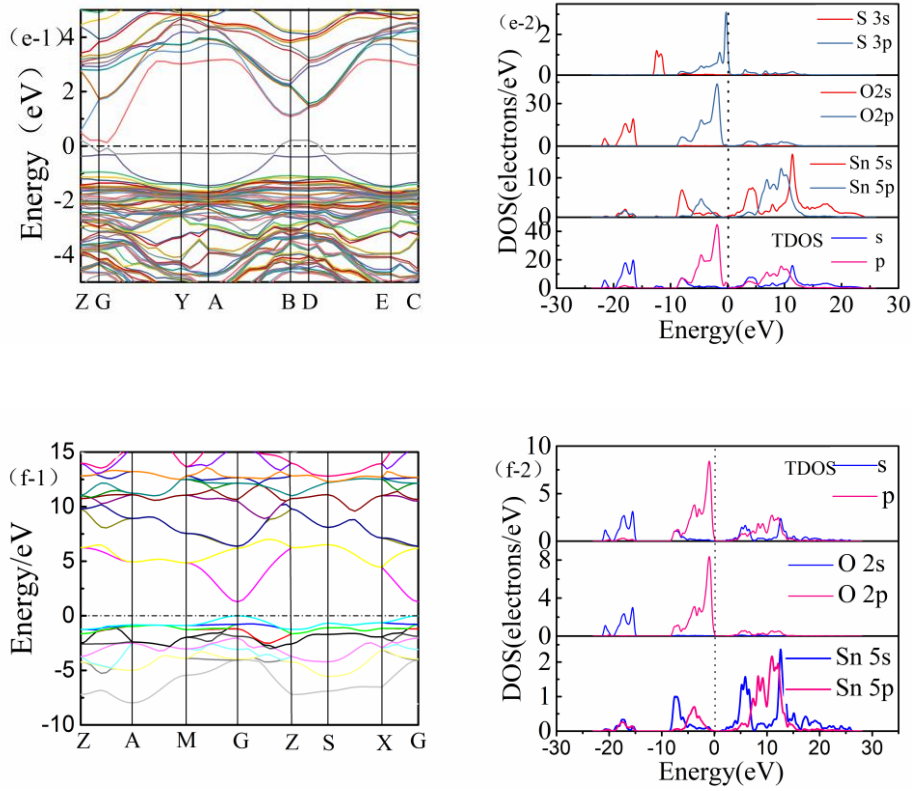


Fig. 2 Energy band structure, total density of States and partial density of states of SnO<sub>2</sub> replacing O atom with nonmetal atom (a) SnO<sub>2</sub>: B (b) SnO<sub>2</sub>: C (c) SnO<sub>2</sub>: F (d) SnO<sub>2</sub>: N (e) SnO<sub>2</sub>: S (f) SnO<sub>2</sub>

For SnO<sub>2</sub>, the Fermi energy level is at the top of the valence band, indicating that the conductivity of SnO<sub>2</sub> is low. The conduction band bottom (CBM) and the valence band top (VBM) are located at the same G point, which is consistent with the calculation results [10][11], indicating that SnO<sub>2</sub> is a direct band gap semiconductor. In this paper, the calculated band gap is 1.28eV, which is consistent with the previous calculation results [12][13][14]. However, the band gap is lower than the experimental value of 3.6eV [15], which is caused by the underestimation of the cross-correlation energy by the GGA function.

The energy of Sn5s orbits and the interaction between Sn5s orbitals and O2p orbitals are overestimated, resulting in a wider valence band and narrower band gap. Band gap and energy band changes do not affect the electronic structure analysis results of SnO<sub>2</sub> crystals. The bandgap value can be modified by the complex variable function method

(DFT + U)<sup>[16]</sup> to obtain a more accurate bandgap value. Although there are still some issues need to be solved with this method, since we mainly discuss the photoelectric properties of element-doped SnO<sub>2</sub>, it is sufficient for us.

The total state density of the SnO<sub>2</sub> crystal shown in Figure 2 illustrates the valence band of the system is divided into two parts, -19.1eV ~ 14.9eV and -8.1eV ~ 0eV. According to the density of partial wave states, the deep energy level is contributed by Sn5s and O2s; the shallow energy level is mainly contributed by O2p, and Sn5s and partially contribute by Sn5p. The shallow energy level -8.1eV ~ -5.8eV is mainly due to Sn5s orbit, and O2p orbit is responsible to the part of -5.8eV ~ 0eV. The conduction band is mainly caused by Sn5s and Sn5p orbits.

It is worth noting that the energy band of SnO<sub>2</sub> doped with non-metallic elements changed a lot. For the non-metallic element doped SnO<sub>2</sub> system, compared with the energy band structure, B-2p, C-2p, S-3p, N-2p orbitals appear in the SnO<sub>2</sub> band gap, which is conducive to enhancing SnO<sub>2</sub> conductivity. The B, F, and S elements cause the Fermi level of the doped crystal to move up. Among them, B and S introduce impurity levels in the SnO<sub>2</sub> band gap, thus the conductivity of the SnO<sub>2</sub> crystal is enhanced. The doping of B atoms leads to more impurity levels in the SnO<sub>2</sub> forbidden band, and the band gap changes greatly, indicating that doping B atoms can adjust the SnO<sub>2</sub> band gap value well.

It can be seen from the partial wave state density diagram that the 2p orbit of the B atom and the 3p orbit of the S atom enter the SnO<sub>2</sub> crystal band gap. With the introduction of F atoms, the Fermi energy level passed through the conduction band of the SnO<sub>2</sub> crystal, and the properties of SnO<sub>2</sub> changed from the semiconductor to the conductor. The analysis of energy band structure of SnO<sub>2</sub> crystal doped with C and N atoms showed the Fermi level crossed the impurity level and enhanced the conductivity of SnO<sub>2</sub> semiconductor. Summing up the analysis, it can be seen that F element doping enhance the conductivity of SnO<sub>2</sub> crystals effectively.

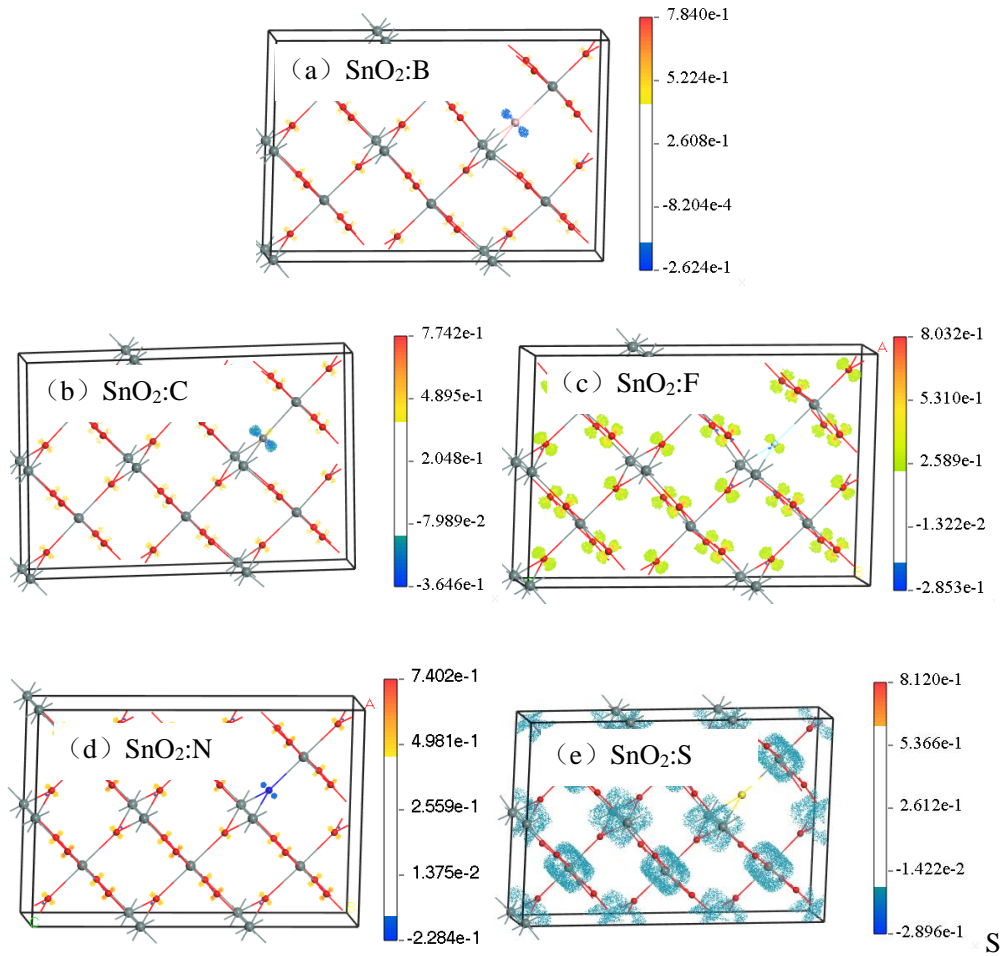


Fig.3 Differential charge density of non-metallic substitution doped SnO<sub>2</sub> film

In order to obtain the information of charge transfer after doping, the secondary differential charge distribution of element doping is calculated and the results were shown in Figure 3. Compared with the O element, the ability of doped atoms to accumulate charge is reduced. This provides more electrons as free carriers, making the system appear metallic. The analysis result is consistent with the analysis result of the energy band structure.

### 3.3 Optical properties

SnO<sub>2</sub> is widely used as a transparent conductive film material, especially in doors and windows, it is also preferred for low-e film glass. The most important performance of low-e glass is the reflectivity in the infrared region. According to the reflectance spectrum of the material, a good adiabatic performance of the material requires the plasma frequency to be close to the visible region. The reflectance spectrum of SnO<sub>2</sub>

doped with non-metallic elements are shown in Figure 4. Analysis of the reflected light spectrum shows that the plasma frequency of SnO<sub>2</sub> doped with F atoms is similar to the visible region, in consequence, it has the highest reflectivity in infrared region. Therefore, SnO<sub>2</sub> doped with F element is the most suitable material for preparing low-e glass thin film.

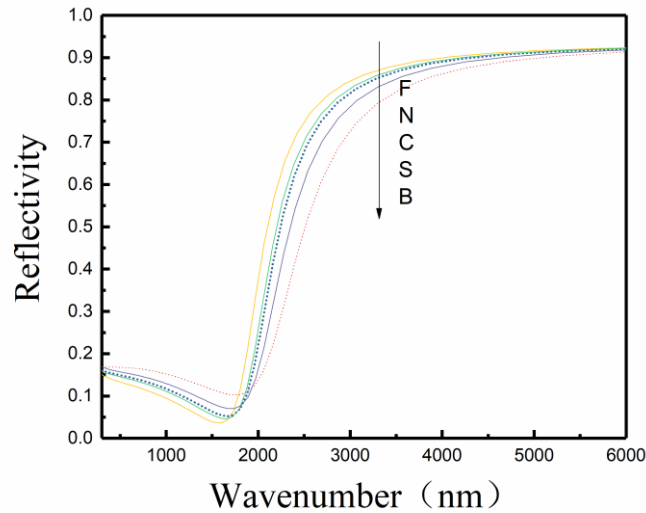


Fig4. The reflection spectrum of SnO<sub>2</sub> of O atom replaced by nonmetal atom

#### 4. Conclusions

Based on first-principles density functional theory, the crystal structure, electronic structure and optical properties of SnO<sub>2</sub> system doped with non-metallic elements were theoretically analyzed. The calculation results confirmed that the doping caused the crystal lattice to expand. The F-doped SnO<sub>2</sub> lattice has the lowest binding energy and is prone to replacement doping. S-doping forms p-type semiconductors, and F-doping forms n-type semiconductors. The optical analysis results revealed that F-doped SnO<sub>2</sub> has the highest reflectivity in the infrared region, and is most suitable as a low-e thin film material to block the ambient temperature.

## References

- [1] Reshmi Krishnan R, Kavitha V S, Santhosh Kumar M C, et al. Properties of Au incorporated  $\text{In}_2\text{O}_3$  films[J]. *Materials Science in Semiconductor Processing*, 2019, 93: 134-147.
- [2] Huo X, Jing s, Liu P, et al. Molybdenum and tungsten doped  $\text{SnO}_2$  transparent conductive thin films with broadband high transmittance between the visible and near-infrared regions[J]. *Crystengcomm*, 2017, 19(30): 4413-4423.
- [3] Untila G G, Kost T N, Chebotareva A B. Fluorine-and tin-doped indium oxide films grown by ultrasonic spray pyrolysis: Characterization and application in bifacial silicon concentrator solar cells[J]. *Solar Energy*, 2018, 159: 173-185.
- [4] Seo S , Jeong S , Park H , et al. Atomic layer deposition for efficient and stable perovskite solar cells[J]. *Chemical Communications*, 2019, 55.
- [5] Dang H P, Luc Q H, Nguyen T T, et al. Eliminating the charge compensation effect in Ga-doped  $\text{SnO}_2$  films by N doping[J]. *Journal of Alloys and Compounds*, 2019, 776: 276-286.
- [6] Fauzia V, Yusnidar M N, Lalasari L H, et al. High figure of merit transparent conducting Sb-doped  $\text{SnO}_2$  thin films prepared via ultrasonic spray pyrolysis[J]. *Journal of Alloys and Compounds*, 2017, 720: 79-85.
- [7] Babu M H, Dev B C, Podder J. Texture coefficient and band gap tailoring of Fe-doped  $\text{SnO}_2$  nanoparticles via thermal spray pyrolysis[J]. *Rare Metals*, 2019: 1-10.
- [8] Sankar C, Ponnuswamy V, Manickam M, et al. Structural, morphological, optical and gas sensing properties of pure and Ce doped  $\text{SnO}_2$  thin films prepared by jet nebulizer spray pyrolysis (JNSP) technique[J]. *Journal of Materials Science: Materials in Electronics*, 2017, 28(6): 4577-4585.
- [9] Liu, Tai-gang & Zhao, Gao-feng & Wang, Yuan-xu. Structural, electronic and magnetic properties of  $\text{GdSi}_n$  ( $n=1\sim 17$ ) clusters: A density functional study[J]. *Physics Letters A*, 2011, 375: 1120-1127.
- [10] Zhang, G., Qin, G., Yu, G., Hu, Q., Fu, H., Shao, C.: Ab initio investigation on a promising transparent conductive oxide, Nb: $\text{SnO}_2$ [J]. *Thin Solid Films*, 2012, 520, 5965–5970.
- [11] Shi, L.-B., Dong, H.-K., Qi, G.-Q.: Density functional theory description of origin of ferromagnetism in Cu doped  $\text{SnO}_2$ [J]. *Magn. Mater*, 2013, 345, 215–221.
- [12] Pressure induced electronic and optical properties of rutile  $\text{SnO}_2$  by first principle

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calculations[J]. *Superlattices & Microstructures*, 2016, 90:236-241.

[13] Li X , Deng R , Li Y , et al. Effect of Mg doping on optical and electrical properties of SnO<sub>2</sub> thin films: An experiment and first-principles study[J]. *Ceramics International*, 2016,42 (4) , 5299-5303

[14] Guo D , Hu C . First-principles study on the electronic structure and optical properties for SnO<sub>2</sub> with oxygen vacancy[J]. *Applied Surface Science*, 2012, 258(18):0-6992.

[15] Dolbec R , Khakani M A E , Serventi A M , et al. Microstructure and physical properties of nanostructured tin oxide thin films grown by means of pulsed laser deposition[J]. *Thin Solid Films*, 2002, 419(1-2):230-236.

[16] Stashans A , Puchaicela P , Rivera R . DFT study of chromium-doped SnO materials[J]. *journal of materials science*, 2014, 49(7):2904-2911.