First-principle Calculation of Effects of Sb Doping on Electrical Conductivity of SnO_2 Transparent Film

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Abstract: In order to investigate the effect of Sb doping on the electrical conductivity of SnO_2, the First-principle calculation of plane wave pseudopotential technology based upon the Density Function Theory(DFT) was performed. The property changes of SnO_2, which Sb doping causes, were studied, such as crystal structure, energy band structure and the state density of the charge. The calculated results revealed that the SnO_2 semiconductor with Sb doping has high conductivity. With the increase of doping concentration, the degeneracy of energy band structure was enhanced, and the energy level of shallow donor impurity is shifted away from the bottom of conduction band.

Key words: SnO_2; First-principles; Electronic structure; Sb-doping
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0 Introduction

SnO_2 is a kind of wide gap semiconductor, which band-gap energy E_g is 3.5 eV at 300 K. It has many properties, such as good fire-retarding, gas and humidity sensitivity, high conductivity and other characteristics (reflecting infrared, lightproof, stable chemical properties)[1-3]. The transparent and conductiv film of SnO_2 is applied widely in display technology and energy transitiv technology, and plays an important role in many photoconductiv film devices[4-5]. Because both of the transmissivity of its visible light and reflectivity of its infrared can reach above 80%, and conductance is $10^3\ \Omega^{-1} \cdot cm^{-1}$, the application prospect of SnO_2 transparent and conductiv film is very wide in the fields of solar cell, thermal reflector, flat display and elcectroluminescent device[6-7].

Though doped SnO_2 film and SnO_2-based ceramics have been researched experimentally and theoretically, its precise optical and electrical properties still await to be profoundly investigated, and the theoretical result cannot guide the experiment at lest. The studies on electron structure, optical and electrical properties have aroused the great interest of many scientists, especially, the theoretical research is rarely reported, so, the studies on electron structure and defect states of SnO_2 crystalline are very important. In recent years, DFT-based first principles have been used to study the optoelectronic property of semiconductors[8]. In this paper, Plane Wave pseudopotential technology of the generalized gradient approximation (GGA) in the frame of DFT theory is adopted to calculate the relation between SnO_2 crystal structure or states of Sb impurity and its conduction theoretically, and the conclusions with directive significance are reached after the theoretical results have been compared with the data of related experiments.

1 Theoretical Model, Calculation Method and Experiment

1.1 Theoretical Model

Ideal SnO_2 crystal is rutile structure, and belongs to P42/MNM (D4H-14) space group, which has cubic symmetry (a and b crystal constant are 47.4 nm, and c is 31.9 nm, all of α, β and γ bonding angles are 90°). The crystal structure of SnO_2 is composed of two groups of sub-lattices including oxygenoctahedroned base (BO_3) with body-centred tetragonal structure that are shifted to 1/2 length along the midpoint link of opposite edges, in which the bond length between center Sn^{4+} and conical point O^{2-} is a little longer than one of the four O^{2-} s in a conical face. The calculation models adopted in this paper are based on the model of SnO_2 supercell (Fig. 1), in which the coordination ratio of Sn^{4+} and O^{2-} is 6∶3. The model of SnO_2 ∶ Sb supercell (Sn replaced with impurity Sb) is given in Fig. 2.

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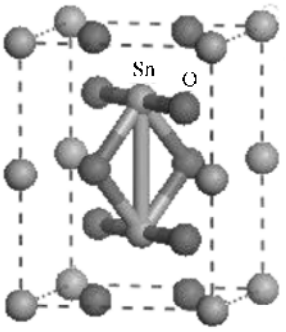

Fig.1 Supercell of SnO_2

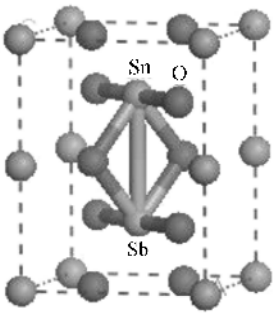

Fig.2 Supercell of Sb-doped SnO_2

1.2 Calculation Method

The analysis of electron structure is mainly the calculation of the energy band structure and the state density of electrons, and the calculated results are discussed, which are accomplished by Castep software package[9] in Materials Studio (MS) 3.2 software. Castep software is a quantum mechanics programme of abinitio calculation based on DFT. Making use of the plane wave pseudopotential technology of general energy that an ion potential is replaced by a pseudopotential, electronic wave function is unfolded with plane wave base groups, the exchange of electron-electron interactions and related potential are revised by local density approximation (LDA) or the generalized gradient approximation (GGA), which is the most advanced and important theoretical simulation in the computer simulation experiments of materials.

The Schrödinger equation of one-electronic motion takes the following form (atom unit) in DFT

$$\left[-\frac{\nabla^2}{2}-\sum_q\frac{Z_q}{|\boldsymbol{r}-\boldsymbol{R}_q|}+\int\frac{\rho(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}'+V_{xc}(\boldsymbol{r})\right]\Phi_i(\boldsymbol{r})=\varepsilon_i\Phi_i(\boldsymbol{r}) \quad (1)$$

$$\rho(\boldsymbol{r})=\sum_i n_i\Phi_i^*(\boldsymbol{r})\Phi_i(\boldsymbol{r}) \quad (2)$$

Where ∇^2, Z_q and $\Phi_i(\boldsymbol{r})$ are respectively Laplace operator, the nuclear charge and one-electron wave function, then n_i and $\rho(\boldsymbol{r})$ show the electronic population of the intrinsic state and multi-electronic density.

In equation (1), the first term shows the efficient kinetic energy of electrons, and the second that adopts norm-conserving pseudo potential is the energy that atomic nucleus attracts electrons. Further, the third is coulomb energy among electrons, and the forth is the exchange and related energy, which is expressed by LDA and GGA.

Periodic boundary terms are adopted in the simulation, so, one-electron orbit wave function meets Bloch law, and is expanded by the plane wave base group as

$$\Phi_i^k(\boldsymbol{r})=\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\sum_g c_i^k(g)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \quad (3)$$

Where g, k and $c_j^k(g)$ are the reciprocal vectors of the primary cell, the wave vectors in the first Brillouin zone and Fourier series of one-electron orbit wave function respectively.

The crystal constants adopted in the calculation are experimental data, in which the basic parameters are set as follows: the truncation energy of plane wave E_{out} is 340eV, the special K points of $4\times4\times2$ Monkorst-park are summed in all Brillouin zone, FFT $30\times30\times54$, computing in reciprocal space.

While self-consistent course terminates, the total energy of the structure convergences to 2×10^{-6} eV/atom, and the force per atom is lower than 0.5 eV/nm. At the same time, the tolerance deviation and stress deviation are respectively 0.02 nm and 0.1Gpa.

1.3 Experiment

After $Sn(OC_2H_5)_2$ solution consists of $SnCl_4$, ethanol and water (which mol ratio is 1∶20∶4), six 0.5mol/L solutions are added respectively to 5%, 6%, 7%, 8%, 9%and 10% (mole per cent) $Sb(OC_2H_5)_3$ (which correspond to add the same as mol weight $SbCl_3$). Having coated on substrates, the dried films have been calcined in the air at 500℃ for 2 hours, and the relative curve of the square resistance of SnO_2 ∶ Sb film and the Sb-doped quantities is gotten in Fig. 3.

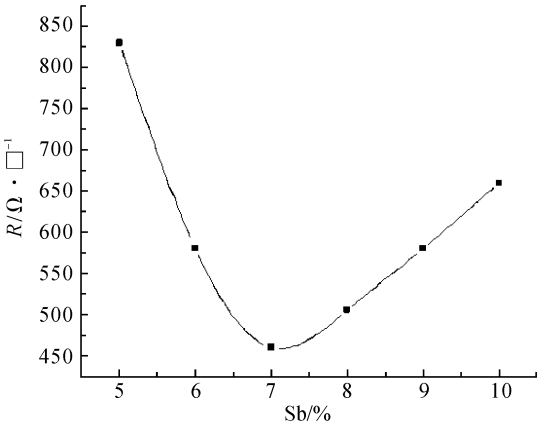

Fig. 3 Curve of the square resistance of Sb-doped SnO_2 films and the Sb-doped quantities

2 Results and discussion

2.1 Electronic structure of intrinsic SnO_2

Electron structures of intrinsic SnO_2, including energy band structure, state density of partial wave and general state density, are calculated at experimental crystal constants. The calculated results are given in Fig. 4 and Fig. 5, which are coincided with the results calculated by

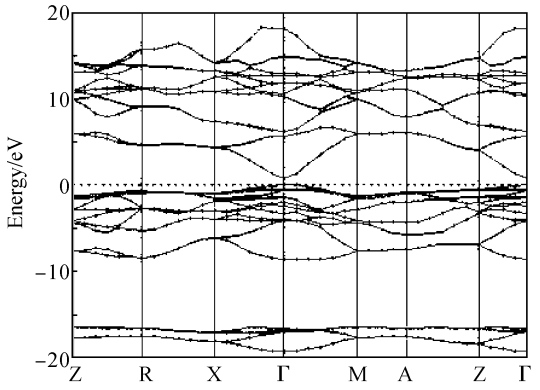

Fig. 4 The Energy band Structure of SnO_2

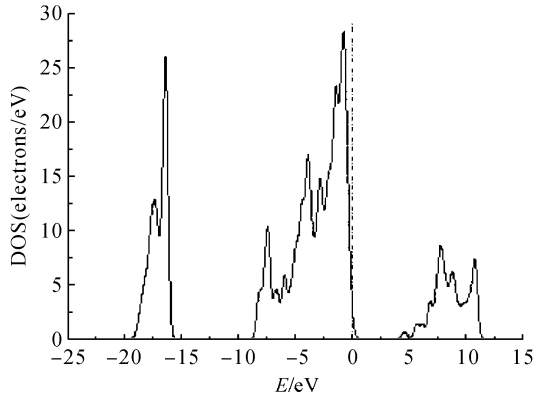

Fig. 5 The total state density of SnO_2

others theoretical methods[10].

The valence band of SnO_2 shown in Fig. 4 can been basically divided two zones : −9.0 eV～−4.0 eV down valence band and −4.0 eV ～ 0.0 eV up valence band.

Fig. 4 shows that SnO_2 is a direct-gap semiconductor, which the bottom of conduction band and top of valence band locate to Γ point of Brillouin zone, and optical gap E_g is 1.1eV.

Combining with the s and p state densities of O and Sn partial waves, we can know that the up valence band and down valence band of SnO_2 are formed respectively from O2p state and Sn5s state. With regard to the contribution of O2s state to -18eV valence band, which isn't discussed here for the interactions with others two valence bands are very small. The conduction band is mainly contributed from Sn5p and Sn5s states, and an electron can obviously jump from Sn5s state to O2p state, which can cause that the gravitation center of local state density on O position shifts toward low energy level. The result reveals that intrinsic SnO_2 is a metal oxide semiconductor, in which ion bond mixes with covalent bond, and the ionicity is stronger than covalent bond. GGA approximation is introduced in calculation, but the calculated gap E_g of SnO_2 is only 1.1eV, which is too small. The reason is from a common problem that the values of E_g calculated with LDA method are all too low. For SnO_2 crystal, Sn5s energy is overestimated in calculation, which makes that the interaction between Sn5s and O2p and the bandwidth of valence band have increased, and causes that the gap reduces. But these results don't affect the theoretical analysis for the electron structure of SnO_2, especially the energy band structure on Γ point accords with the experimental datum[10]. In order to make the gap width approach to the experimental value, so, scissors are set to 2.67eV in later calculation. In the energy band structure, the energy level of down valence band from Sn5s changes very slowly, and the energy level of up valence band from O2p does more smoothly than the change of conduction band, which indicates that the hole in the valence band has a large effective mass, and SnO_2 can easily form n-type semiconductor.

2.2 Relation between electron structure and its conductivity of SnO_2 : Sb

Based on above Sb-doped experiments, the simulation is operated theoretically. The used Supercells and the Sb-doped mol ratios are given in Tab. 1.

Tab. 1 The Supercells and the Sb-doped Mol Ratios

	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ
Supercells	1×2×3	2×2×3	2×2×2	1×2×3	1×2×2
Sb-doped Mol Ratios	0	4.17%	6.25%	8.3%	12.5%

The energy bands shown in Fig. 6, Fig. 7, Fig. 8 and Fig. 9 have been degenerated, and the Fermienergy level moves into the conduction band. At the same time, an energy band under down valence band is introduced whose width is about 0.1eV. Compared with the energy band structure of intrinsic SnO_2, the energy band is reduced with the increase of Sb-doped concentration. In Sb-doped SnO_2, the optical gap E_g is broaden, and the data E_g are as follows: 3.4783eV of intrinsic SnO_2, 0.6359eV of SnO_2 with 4.17% impurity, 0.8478eV of SnO_2 with 6.25% impurity, 0.8696 of SnO_2 with 8.3% impurity, and 0.9783 eV of SnO_2 with 12.5% impurity. The broadened reason is mainly that high doping concentration causes free carriers have changed the gap of SnO_2 in two aspects. In one hand, high concentration carriers have brought that the Fermi energy level enters the conduction band, and produced the so-called Burstein-Moss movement, which the edge of optical absorption is reduced so that the gap is widened . In the other

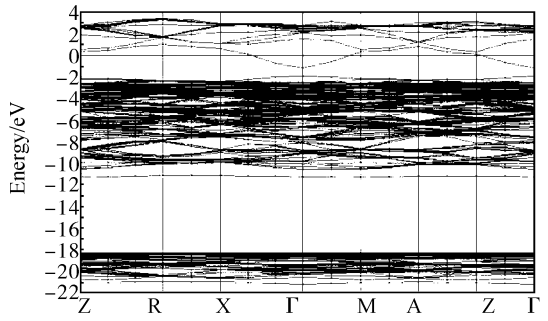

Fig. 6 The energy band structure of SnO_2 with Sb-doping SnO_2 by 4.17%

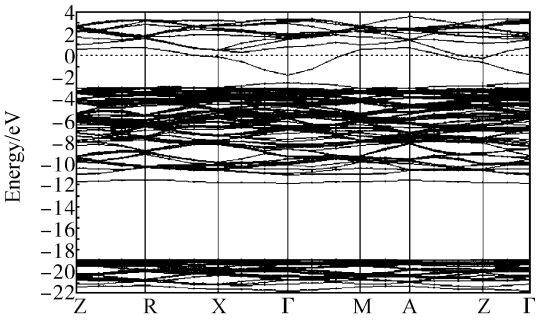

Fig. 7 The energy band structure of SnO_2 with Sb-doping SnO_2 by 6.25%

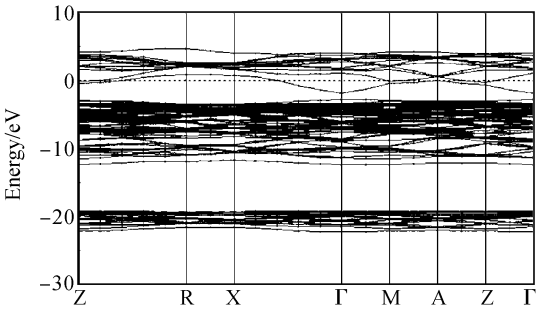

Fig. 8 The energy band structure of SnO_2 with Sb-doping SnO_2 by 8.3%

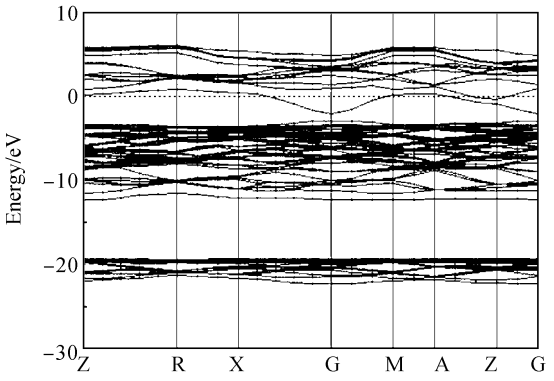

Fig. 9 The energy band structure of SnO_2 with Sb-doping SnO_2 by 12.5%

hand, the interactions among carriers generate the multi-body effect, or the overlapping between impurity band and defect band makes the gap narrow. Moreover, the effect of the former is smaller than one of the latter, which is known by calculating. In a word, the optical band gap could diminish generally with the increase of carrier concentration.

The formula of optical gap is

$$E_g = E_{go} + \Delta E_g^{BM} - \Delta E_g^{W} \tag{4}$$

Where E_{go} is the band gap of intrinsic material , and ΔE_g^{BM} is the Burstein-Moss movement. ΔE_g^{W} is the reducing value downward of the conduction band generated by multi-body effect among electrons, which is derived from Burstein-Moss and Woff theories

$$\Delta E_g^{BM} = \left(\frac{h^2}{8m^*}\right) \cdot \left(\frac{3n}{\pi}\right)^{\frac{2}{3}} (\text{eV}) \tag{5}$$

$$\Delta E_g^{W} = \frac{l}{2\pi\varepsilon_0\varepsilon_r}\left(\frac{3n}{\pi}\right)^{\frac{1}{3}} (\text{eV}) \tag{6}$$

Considered the partial wave state density of s and p states in Sb with its energy band structure pattern, it is found that there is a 1eV-width band in 12eV point, which is thought to be generated from Sb5s. After general state density and partial wave state density have been analyzed, there are a great deal of overplus electrons in the bottom of conduction band, which induce Fermi-energy level to enter conduction band, so that SnO_2 : Sb crystal possesses the character of a degenerate semiconductor. The dispersion of valence band is pricked up while Sb-doped concentration is increased. The reason is that impurity atoms close up each other in high impurity concentration, what the electron wave functions that are bound up by Sb ion prominently overlap causes that the communization movement of Sb5s and O2p orbital electrons is reinforced, and the valence band is widened. Contrasted partial wave state density of Sb with one of Sn, the effect of Sb impurity on the conduction band of SnO_2 is as follows: the state density of Fermi energy level E_F that moves into conduction band originates mainly from the contribution of Sb atom, to which the contribution of Sn atom is very small. So, Sb element is the adequate doping to prepare stable n-type and low-resistance SnO_2 semiconductor.

Because there are a great deal of overplus electrons in the bottom of conduction band while the Fermi energy level enters into the conduction band, the degenerate semiconductor is described only with Fermi distribution, but classical Boltzmann distribution cannot be used. Thus, the energy level of conduction band happens to zigzag and overlap gradually while Sb doping concentration increases. Although a great deal of electrons silt at the bottom of conduction band, its conductivity changes with Sb-doped quantities,

which is given in Fig. 3, and its resistance exists a minimum. It is known from semiconductor theory that Sb doping belongs to substitutional impurity. In fact, Sb atoms substitute Sn atoms on normal lattice points, which generate extra free electrons. As a result, the larger the doped quantity is, the more Sn atoms are replaced, and the more electrons are released out. Thus Fermi energy level enters conduction band, a great lot of overplus electrons in the bottom of conduction band cause that the square resistance of the film decreases. While the impurity concentration is increased by a definite value, the populations of doped atoms in grains and in grain boundaries go to the saturation, and the scatterings of ionized impurities and lattice defects start to reinforce with the increase of doped concentration, which leads to that the mobilities of carriers drop. Furthermore, the square resistance of the film slowly rises. The results of simulation calculation are shown in Fig. 5, Fig. 10, Fig. 11, Fig. 12 and Fig. 13, the electron structure pattern of impurity state in SnO_2 is analyzed, Sb-doped concentrations such as 4.17%, 6.25%, 8.3%, and12.5% are all recognized to belong to low-doped quantities, by which the energy level E_d of shallow donor has generated under the bottom of conduction band, but has moved further away from the bottom with the increase of doped quantities. For example, E_d are −0.030 90 eV, −0.689 69 eV,

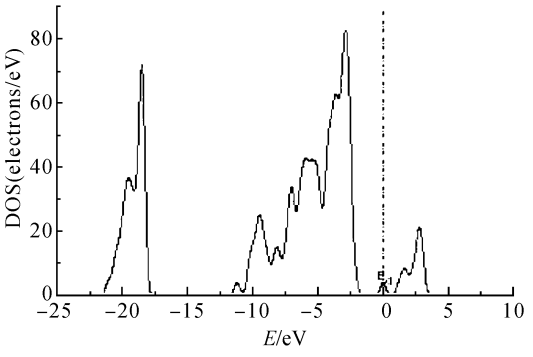

Fig. 10 The total state density of with Sb-doping by 4.17%

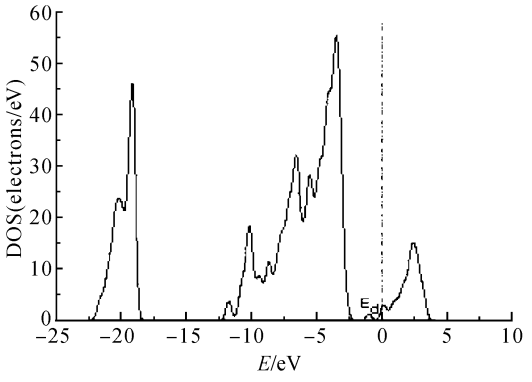

Fig. 11 The total state density of with Sb-doping by 6.25%

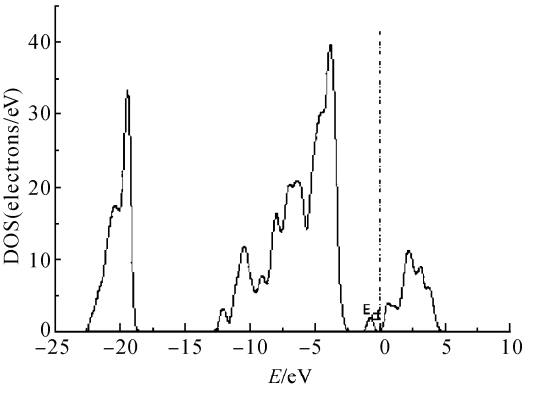

Fig. 12 The total state density of with Sb-doping by 8.3%

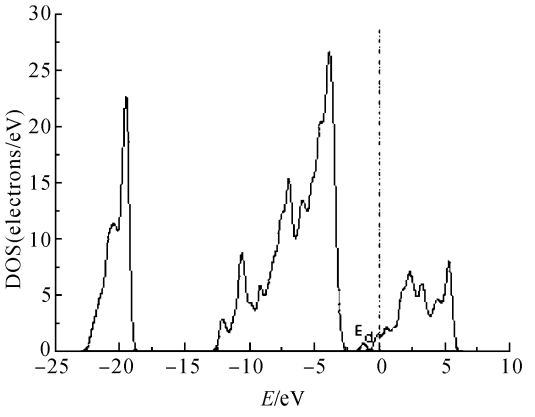

Fig. 13 The total state density of with Sb-doping by 12.5%

−0.998 44 eV and −1.210 44 eV respectively while Sb-doped concentrations are 4.17%, 6.25%, 8.3% and 12.5%. According to semiconductor physics, the closer the energy level of shallow donor is to the bottom of conduction band, and the more easily the electrons in E_d jump to the conduction band and become conduction carriers. It is obvious that conduction capability of SnO_2 : Sb wears off with the increase of Sb-doped concentration, which is basically coincident to the right part of the minimum in the curve of Fig. 3. The simulation calculation for the left part of the minimum in the curve of Fig. 3 brings out relatively great difficulty due to small doping concentration, so, it isn't discussed here.

3 Conclusion

The internal relation of electron structure with conduction capability in SnO_2 : Sb and n-typt doping mechanism are researched by the first principles based on DFT, the simulation results are as follows:

1) SnO_2 is theoretically previewed as a kind of direct-gap semiconductor, whose both of the bottom of conduction band and top of valence band lie to the center point Γ in Brillouin zone. At the same time, SnO_2 formed in natural condition is n-

type semiconductor.

2) A narrow and shallow energy level of the donor is formed by Sb doping in the gap, and degeneration of the energy band has aggravated with the increase of Sb-doped concentration, which causes that the energy level of the shallow donor moves away from the bottom of the conduction band. The result explains that the conduction capability of SnO_2 : Sb wears off, which basically accords with the experimental curve.

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Sb 掺杂对透明 SnO_2 薄膜导电性能影响的第一性原理计算

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摘　要：本文根据密度泛函理论(DFT)，采用第一性原理平面波赝势方法，计算了 Sb 掺杂对透明导电薄膜 SnO_2 电子结构及导电性能的影响，讨论了掺杂下 SnO_2 晶体的结构变化、能带结构、电子态密度. 计算结果表明，Sb 掺杂的 SnO_2 具有高的电导率，且随着掺杂浓度的增加，能带简并化加剧，浅施主杂质能级向远离导带底方向移动.

关键词：SnO_2；第一性原理；电子结构；掺杂

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