

Theoretical Study on Rare Earth Doped AgSnO_2 Contact Materials by First-principles

CAI Yanan, WANG Jingqin*, ZHAO Caitian

(1. Electrical Apparatus Institute, Hebei University of Technology, Tianjin 300130, China)

Abstract: For AgSnO_2 contact materials, Ag has good electrical conductivity while SnO_2 has high thermal stability. However, SnO_2 , despite of a semiconductor with a wide band gap, is nearly a non-conducting compound, leading to an increase in the resistance of AgSnO_2 . By doping SnO_2 with other conductive metals, the electrical properties of AgSnO_2 can be effectively improved. In the present theoretical study based on the first-principles, the electric structure of SnO_2 doped with La Ce and Nd was analyzed, and the crystal structure, band structure and density of states of the intrinsic SnO_2 and doped SnO_2 , were compared. The crystal structure shows that the lattice distortion caused by the rare earth is related to the covalent radius of the doping atoms. The conduction band of the doped SnO_2 shifts to the lower energy level, as indicated by the band structure, resulting in a narrow bad gap and improved electrical conductivity. SnO_2 doped with La has a minimum band gap. The density of states reveals that the unique electronic state on f-orbits of the rare earth has a great contribution to the conduction band at the Fermi level. The density of states of La-doped SnO_2 is the maximum.

Key words: contact materials; electrical conductivity; first-principles; rare earth; doping; SnO_2

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稀土元素掺杂 AgSnO_2 触头材料的第一性原理理论研究

蔡亚楠, 王景芹*, 赵彩甜

(河北工业大学 电器研究所, 天津 300130)

摘要: AgSnO_2 触头材料中 Ag 具有良好的导电性, SnO_2 具有较高的热稳定性。但是, SnO_2 是一种宽禁带半导体, 近乎绝缘, 使得 AgSnO_2 触头材料的电阻较大。通过对 SnO_2 进行掺杂, 使 SnO_2 由绝缘改性为导电, 能有效改善 AgSnO_2 的电性能。采用第一性原理研究了稀土元素 La、Ce、Nd 掺杂后的电子结构, 对纯 SnO_2 和掺杂 SnO_2 的晶体结构、能带结构、态密度进行了分析对比。晶格数据表明, 稀土元素掺杂 SnO_2 引起的晶格畸变与掺杂原子的共价半径大小有关。能带结构表明, 稀土掺杂可使 SnO_2 的导带向低能端移动, 带隙变窄, 即导电性提高, 且 La 掺杂时的带隙最小。电子态密度表明, 稀土元素特有的 f 态电子对费米能级处的导带贡献很大, 即稀土元素掺杂能提高 AgSnO_2 触头材料的导电性, 且 La 掺杂时的费米能级处的态密度值最大。

关键词: 触头材料; 导电性; 第一性原理; 稀土; 掺杂; SnO_2

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第一作者: 蔡亚楠, 女, 硕士研究生, 研究方向: 电器电接触。E-mail: 1063744459@qq.com

*通讯作者: 王景芹, 女, 教授, 研究方向: 电器电接触。E-mail: jqwang@hebut.edu.cn

The electrical properties of contact materials directly affect the working condition of contact elements, thereby affecting the overall reliability of the electrical and electronic systems. In 1939, F. R. Hensel developed AgCdO contact material with low contact resistance and high anti-welding ability^[1]. Then, AgCdO contact material has been studied in-depth and used widely in low-voltage electrical equipment. However, the studies found that, under high temperature, CdO is decomposed to produce poisonous Cd vapor, which threatens human health and pollutes atmospheric environment. In 2003, European Union issued the ROHS and WEEE to limit the use of hazardous substances, such as Cd, in electrical and electronic equipment^[2]. So, people began to research more secure and more excellent electrical contact materials. Then new none-pollution AgSnO₂ contact material arises at the historic moment. It's good arc erosion resistance, abrasion resistance and welding resistance make it be the biggest promising to replace the "universal contact" - AgCdO. However, SnO₂, an important component of AgSnO₂ contact material, is a kind of wide band gap semiconductor, near insulation, which induces the resistance of the contact material to increase and the temperature to rise, thereby resulting in reducing electric life^[3-5]. Experimental research shows that the element doping is an effective method to improve the electric conductivity of SnO₂. Element doping becomes a new researching spot in the field of contact materials, making the AgSnO₂ contact material have a broader application prospect^[6-7].

In recent years, there are more and more researches on elements doping and experimental preparation of new AgSnO₂ contact material. Yu et al.^[8] pointed out that SnO₂ doped with V, Cr showed semi-metallic properties. Shan et al.^[9] found that in Ce doped SnO₂, the 4f orbit of Ce moved into the conduction band, and induced the bottom of the conduction band to move to the low energy end, then electrical conductivity increased. Rare earth elements have unique 4f

electronic structure. Due to the shielding of the outer 5s and 5p orbits, temperature and crystal field have little impact on the 4f electrons' transition, which is a new hot-spot in the study of the doping SnO₂^[10]. Zhang et al.^[11] found that in La, Sm, Gd, Dy, Ho, Lu doped BaTiO₃, fermi level got into the conduction band, then the system presented higher electrical conductivity. Zhu et al.^[12-13] successfully developed new AgSnO₂ / CeO₂ and AgSnO₂ / La₂O₃, and verified that the addition of CeO₂ and La₂O₃ effectively reduced the arc parameters of contact materials by experiments.

In this article, we use the Materials Studio software, choose La, Ce and Nd rare earth elements to dope SnO₂, and use the first-principles based on density functional theory (DFT) to calculate. By analyzing geometry optimization results, band structures and density of states of doped systems, we theoretically prove that La, Ce, Nd can improve the conductivity of SnO₂ to a certain extent, so they can improve AgSnO₂ electrical property of contact material. It provides a theoretical basis for the future research and development of AgSnO₂ contact material.

1 The model and method

1.1 Theoretical model of rare earth doped SnO₂

Based on the experimental results, the lattice constants of SnO₂ - component of AgSnO₂ contact material, are $a=b=0.4737$ nm, $c=0.3186$ nm. The original cell contains two Sn atoms and four O atoms. The standard SnO₂ structure is taken from the structure library of Materials Studio^[14], which is rutile, and it's space group is P42/mnm. Fig.1 is the 1×2×2 supercell of SnO₂. Gray parts represent Sn atoms and red parts represent O atoms. X atom (X represent La, Ce and Nd) is chosen to replace the center Sn atoms in intrinsic SnO₂ structure (Fig.1(a)) in turn, then doped SnO₂ structure (Fig.1(b)) is constructed.

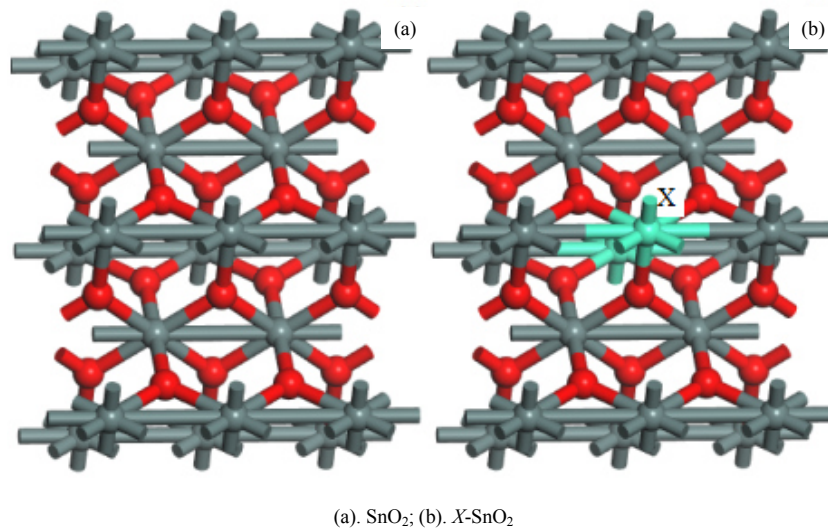


Fig.1 The supercell (1×2×2)of SnO₂

图 1 SnO₂ 的 1×2×2 型超晶胞

1.2 Method by first-principles for calculation

In this paper, the CASTEP software is used to calculate the structure. Firstly, the structure is geometrically optimized for finding the most stable point of the crystal structure, and then energy calculation can be carried out from two aspects of band structure and density of states. The periodic boundary conditions, the generalized gradient approximation(GGA) and the PBE were used^[15-16]. Calculation parameters are chosen as follows: the energy cut-off of plane wave takes 300 eV, forces acted on each atom takes not greater than 0.05 eV, internal stress takes not greater than 0.1 GPa and Monkhorst-Pack mesh of Brillouin-Zone sampling

takes 2×3×4. The atomic configuration for O, Sn, La, Ce and Nd are 2s²2p⁴, 5s²5p², 5s²5p⁶5d¹6s², 4f¹5s²5p⁶5d¹6s² and 4f⁴5s²5p⁶6s² respectively, and calculation are all conducted in the reciprocal space.

2 Calculation results

2.1 Geometry structure

In table 1, the equilibrium lattice constants of pure SnO₂ and doped SnO₂ in AgSnO₂ contact material after geometry optimization, bond length between doping rare earth elements and different O atoms, single point, and atomic radius are given.

Tab.1 The Structure of Pure SnO₂ and Doped SnO₂ after Optimization

表 1 纯 SnO₂ 和掺杂 SnO₂ 优化后的几何结构

System	Lattice parameters/nm			Bond lengths/nm	Single point energy/eV	Atomic radius/nm
	<i>a</i>	<i>b</i>	<i>c</i>			
SnO ₂	0.4737	0.4737	0.3186	Sn-O1: 0.2052; Sn-O2: 0.2055	-1936.958	0.1400
SnO ₂ -La	0.5089	0.5079	0.3406	La-O1: 0.2386; La-O2: 0.2487	-2129.750	0.1810
SnO ₂ -Ce	0.5028	0.5009	0.3341	Ce-O1: 0.2236; Ce-O2: 0.2294	-2181.248	0.1711
SnO ₂ -Nd	0.4984	0.5009	0.3307	Nd-O1: 0.2208; Nd-O2: 0.2258	-2305.542	0.1710

From table 1 it can be seen that rare earth doping induces the lattice distortion, however, due to the lattice constants are similar with experimental value given above, optimization is considered correct, and

the next phase of energy analysis can be taken. The main reason of distortion is that the radius of La, Ce, Nd is greater than that of Sn. The degree of lattice distortion is different. The lattice constant and bond

length of La doped SnO_2 are the biggest, while that of Nd doped SnO_2 are the smallest, which is consistent with the atomic radius of La, Ce, Nd gradual decrease. Compared pure SnO_2 and doped SnO_2 , single point of doped SnO_2 reduces, so that stability enhances. Compared La- SnO_2 , Ce- SnO_2 and Nd- SnO_2 , single point decreases, so that stability enhances in turn.

2.2 Electronic structure

Fig.2 shows energy band structure of pure SnO_2 (Fig.2(a)) and doped SnO_2 (Fig.2(b)) in AgSnO_2 contact material. Fig.2(a) shows that the bottom of the conduction band and the top of the valence band of SnO_2 are both located in the Brillouin Zone G, so SnO_2 is a direct band-gap semiconductor. 0~20 eV region is the conduction band, -10~0 eV region is the

valence band near the Fermi level and -20~15 eV region is also valence band, which is so smooth and dense that it does not have much value of reading. The band of pure SnO_2 is sparse and fluctuate and the forbidden band width of it is 1.005 eV, which is smaller, compared with the experimental value of 3.6 eV. It mainly because by the density functional theory, the universality of the calculated value of E_g is low and the energy of Sn 5s is overestimated^[17]. Though there is a small pity, the method is all accepted and used, because the band structure accords with the physical truth, so it is still meaningful to study the relative band-gap change of doped SnO_2 under the same parameters.

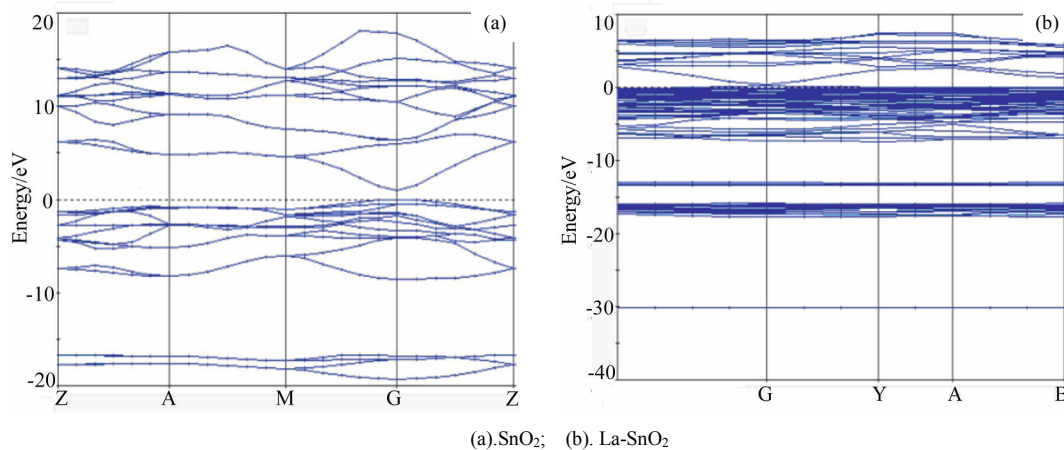


Fig.2 The band structure of SnO_2

图2 SnO_2 的能带图

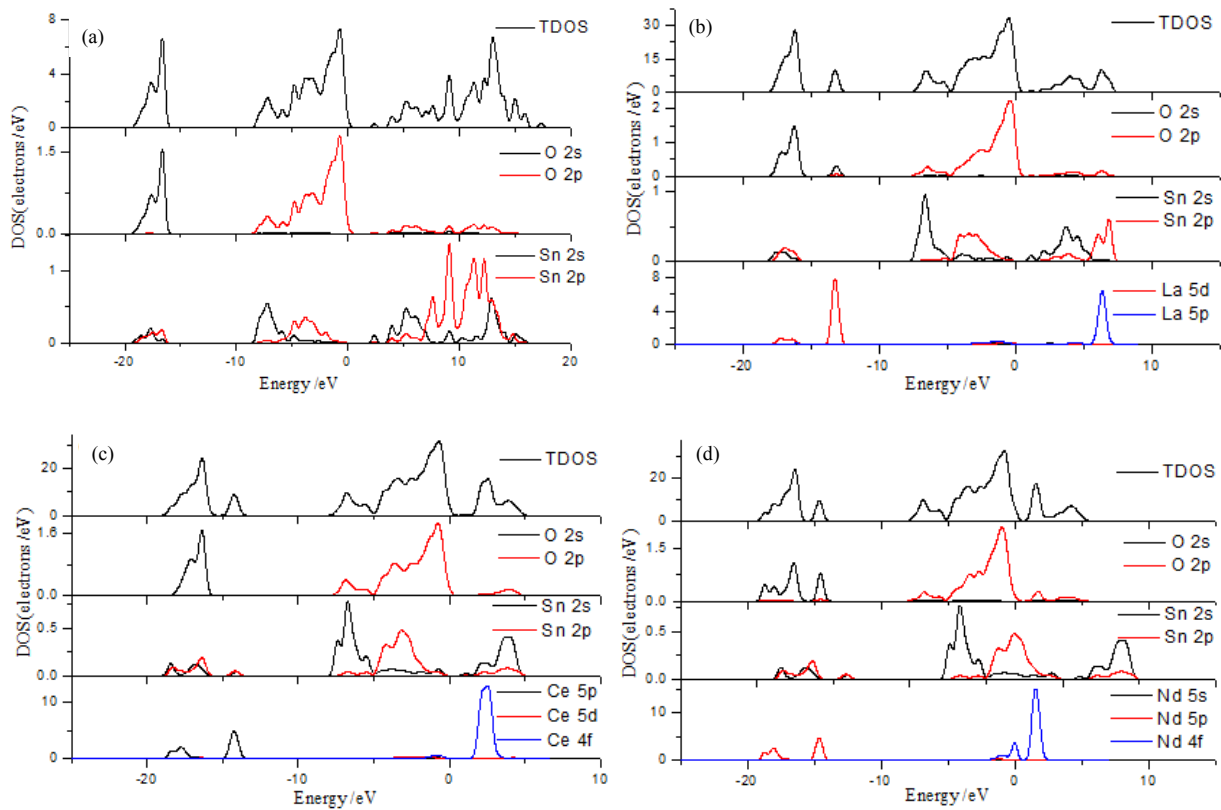
The simulation results show that the band structures of La, Ce, Nd doped SnO_2 are similar, therefore, Fig.2(b) only gives the band structure of typical La doped SnO_2 , which shows that the bottom of the conduction band and the top of the valence band are still located in the Brillouin Zone G, and there is no introduction of intermediate level between the top of the valence band and bottom of the conduction band, but there is an introduction of a new and more narrow band in -15~-10 eV region, which is usually called impurity state. Compared with the pure SnO_2 , the band structures of La, Ce, Nd doped SnO_2 become more intense and less fluctuate, which indicates enhancement of electronic locality and increase of

effective mass. After doping, the conduction band moves to the lower end, seen from the ordinate of the two figures, which suggests that the doping elements lead to stronger interaction between different atoms, narrower band gap and less energy needed by the electrons to excite from the valence band to the conduction band. Calculation results show that band gaps of La, Ce, Nd doped SnO_2 are 0.2242, 0.4838 and 0.6150 eV respectively, which are all smaller than that of pure SnO_2 - 1.005 eV. This phenomenon indicates that the electrical conductivity is improved. La, Ce doping reduces band gap more, while Nd doping reduces less, which is consistent with single point of Nd- SnO_2 is the minimum in table 1. Compare La, Ce,

Nd doped structure, we found a trend of gradual increase in band gap, which indicates electrical conductivity of the doped contact materials gradually decrease. So under the same doping amount, the electrical conductivity of La doped AgSnO_2 contact material is the best, which is consistent with the experimental result by alloy powder method^[18].

For further analysis of the electrical conductivity of three kinds of rare earth doped AgSnO_2 contact materials, Fig.3 shows the the total density of states

(TDOS) and partial wave density of states (PDOS) of pure SnO_2 (Fig.3(a)), La- SnO_2 (Fig.3(b)), Ce- SnO_2 (Fig.3(c)) and Nd- SnO_2 (Fig.3(d)). In pure SnO_2 , -10~0 eV region is the valence band, and the state density of the top of the valence band is mainly contributed by O 2s and O 2p state, while 0~20 eV region is the conduction band, and the state density of the bottom of the conduction band is mainly contributed by Sn 5s and Sn 5p state.



(a). SnO_2 ; (b). La- SnO_2 ; (c). Ce- SnO_2 ; (d). Nd- SnO_2

Fig.3 The density of states of SnO_2

图 3 SnO_2 的态密度图

After doping, the state density diagrams are very similar. Fig.3(b), (c), (d) show that the DOS of doped SnO_2 all across the Fermi level, which indicates metallicity and increase of the conductivity. In -15~-10 eV region, there is a new waveform emerging, which is primarily induced by the 5p state of La, 5p state of Ce and 5p state of Nd, respectively, seen from PDOS. The valence band near the Fermi level is still contributed by the 2p state of O, and electronic state

changed little, so the top of valence band change little. While the conduction band near Fermi level is partly contributed by the 5s and 5p state of Sn, partly by 5d state of La, 4f state of Ce and 4f state of Nd, obviously, 4f state of Ce and 4f state of Nd contribute more than 5d state of La, seen from PDOS of Fig.3(b), (c), (d). In addition, the conduction band-gap (0~5 eV) of doped SnO_2 significantly reduces, compared with the conduction band-gap (0~20 eV) of pure SnO_2 ,

meaning enhancement of locality.

For further verification of that the doping rare earth elements can improve the electrical conductivity of AgSnO₂ contact material, table 2 lists the state density of pure SnO₂ and doped SnO₂ in Fermi surface. And it is obviously when the latter is bigger, which illustrates that the three doping elements all can improve the electrical conductivity of AgSnO₂ contact material. The state density of La doped SnO₂ in Fermi surface is the largest, which illustrates La doping can enhance electrical conductivity most, which is consistent with the former results.

Tab.2 The density of states at the Fermi level of the pure and doped SnO₂

表 2 纯 SnO₂ 和掺杂 SnO₂ 在费米面的态密度值 /eV

SnO ₂	SnO ₂ -La	SnO ₂ -Ce	SnO ₂ -Nd
0.574	1.667	0.830	0.753

In order to see the change of electron transfer, table 3 lists the electron gain and loss of Sn and doping element X. The E_X refers to the gain number of X, E_{Sn} refers to the gain number of Sn near X, E_O refers to the gain number of O near former Sn.

Tab.3 The electron transfer of the pure and doped SnO₂

表 3 纯 SnO₂ 和掺杂 SnO₂ 的电子转移

Doped element	$E_X(e)$	$E_{Sn}(e)$	$E_O(e)$
Intrinsic SnO ₂	-1.90	-1.90	0.95
La	-1.76	-1.77	0.87
Ce	-1.38	-1.79	0.89
Nd	-1.18	-1.81	0.90

Seen from table 3, the electron transfer of pure SnO₂ and doped SnO₂ is different. Rare earth doping leads to electron loss of both Sn and X, but X loses less than connected X. The result is consistent with that the conduction band is mainly contributed by Sn, partly by X in the state density figure. O atoms all gain electrons, partly from rare earth atom. In the three kinds of mixed system, La loses electron most and Nd loses electron least, which is consistent with the former justification that La doped SnO₂ has worst stable structure and strongest electrical conductivity.

3 Conclusion

In this paper, by using Materials Studio software, the pure SnO₂ and rare earth La, Ce, Nd doped SnO₂ in AgSnO₂ contact material are calculated by first-principles, including structure optimization and energy calculation. The conclusions are as follows:

1) The pure SnO₂ is a kind of direct band-gap semiconductor, with 1.005 eV band gap and poor conductivity. After doping, band gap decreases, valence band crosses the Fermi surface, conduction band width narrows and state density in Fermi surface increases. They illustrate that La, Ce, Nd doping elements can, to a certain extent, improve the electrical conductivity of AgSnO₂ contact material.

2) Contrast the band gap of three doped structures (0.2242, 0.4838 and 0.6150 eV) and the state density in the Fermi surface (1.667, 0.830 and 0.753 eV), we get the conclusion that, under the same condition, when doping La, conductivity is best.

3) With this method introduced in this paper, all kinds of elements that may improve AgSnO₂ electrical conductivity can be found. This method provide blueprint for research and development of new contact materials, improve the design efficiency and cost savings.

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