Research on Magnetic Property of Environmental Friendly Material SnO₂: Mn, S

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Abstract. Tin dioxide (SnO₂) is a commonly known material with the rutile structure of wide band gap n-type semiconductor which is widely used like ZnO common oxide materials in daily life. But comparing with ZnO, it has a wider band gap (about 3.6 eV), and a higher exciton binding energy 130 meV. Because of its excellent optical, electrical and other excellent physical and chemical characteristics, SnO₂ has been widely adapted in thermoelectric film, gas sensor, photovoltaic devices, magnetic materials, and other related fields. A large number of theories and experiments illustrate that, after the proper doping, the remarkable improvements can be achieved. Based on the first principle, we investigated the photoelectric properties and magnetic properties when the Mn and S were doped in SnO₂. It was shown by calculation that a Mn atom provides 1.52 μ_B magnetic moment and a S atom provides 0.06 μ_B , while O and Sn atoms rarely contribute to the system. In the system the magnetism is mainly derived from the Mn-3d electronic spin polarization.

1 Introduction

As an environmental friendly material, SnO₂ has a rutile structure and is also an n-type wide bandgap semiconductor with a band gap of 3.6 eV. In an experiment, due to the successful preparation of TiO₂ diluted magnetic semiconductor [1], people began to broaden their horizons to other oxide semiconductor materials, such as tin dioxide we are going to talk about here. Since then, people began to study SnO₂ dilute magnetic semiconductors both experimentally and theoretically. Dietl and his collaborators used pulsed laser deposition (PLD) technology to grow Co-doped SnO₂ thin film samples [2-4]. They found that when the Co doping concentration is less than 3%, the sample film will show ferromagnetism and be highly transparent. The Curie temperature of the sample is close to 650 K, the saturation magnetization is about $7.5 \pm 0.5 \mu_B/\text{Co}$, and the magnetic moments in the Co and Co clusters are $1.67 \mu_B/\text{Co}$ and $2.1 \mu_B/\text{Co}$, respectively. It can be seen that the film The cobalt magnetic moment of the sample is much larger than that of cobalt and cobalt clusters and that of cobalt in other cobalt oxides, but there is a little regret that its magnetization will rapidly weaken as the Co concentration increases.

Fukumura et al. also successfully prepared iron-doped SnO₂ semiconductor materials by pulsed laser deposition technology, and the prepared samples showed ferromagnetic and highly transparent characteristics [5]. Fitzgerald and his collaborators took the work one step further and found room temperature ferromagnetism in Sn_{1-x}M_xO₂ (M= Mn, Fe, Co, x=0.05) semiconductor materials [6]. Fitzgerald and his collaborators later studied the use of PLD to prepare transition metal doped SnO₂ [7-

9].

Menzel and his collaborators used magnetron sputtering to prepare Co-doped SnO₂ thin film samples on a silicon substrate. They doped the thin film samples at a concentration of 3%, 5%, and 7%, respectively. Among the three samples prepared All have room temperature ferromagnetism, and the cluster size of Co in the sample is less than 1 nm [10]. Mishra et al. studied Fe-doped SnO₂ nanoparticles, and the experimental results showed that the sample showed paramagnetism, and the Fe³⁺ in the sample was in a paramagnetic state [11-15].

Mn is also often used as a transition metal cation to dope SnO₂ crystals to study its magnetic modification effect. Yu Li, Zheng Guang and others mentioned that the magnetic moment is mainly derived from the 3d orbital of the doped element in the calculation of Mn doped SnO₂. Spin polarization of electrons [16]. The doping of S can introduce oxygen vacancies, and the effect of the presence of oxygen vacancies on the magnetic properties of the system cannot be ignored. As there is no report about the co-doping of Mn and S with SnO₂, this article will explore the co-doping of Mn and S with SnO₂.

2 Calculation method and model

In this paper, we use the software package to calculate. The specific calculation parameters are set as follows: select the PBE exchange correlation potential under the generalized gradient approximation (GGA), set the cut off energy to 300 eV, set the k-point grid to $4 \times 4 \times 6$, and set the initial Spin is set to 3. When the total energy change of the system stabilizes within 1.0×10^{-5} eV, the self-consistent field (SCF) of the electronic structure stops calculating. In the calculation process, the selected valence electron

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configurations of tin, oxygen, manganese and sulfur atoms are ($5s^25p^2$), ($2s^22p^2$), ($3d^54s^2$) and ($3s^23p^2$) respectively. The calculation model is shown in Figure 1. This $2 \times 2 \times 2$ supercell has 48 atoms in total (15 Sn atoms, 31 O atoms, 1 Mn atom and 1 S atom). The doping method is that one Mn atom replaces one Sn atom, and one S atom replaces one O atom. The doping concentrations of Mn and S are 6.25% and 3.125%, respectively.

Fig. 1. The model graph Cu, S co-doping SnO₂.

3 Results and discussion

3.1 Magnetic properties

According to the above model and calculation parameters, this paper calculates the Mn and S co-doped SnO₂ system. After optimizing the supercell, the lattice constant is divided into $a=4.847$ Å, $c=3.316$ Å, and the magnetic moment distribution of the system is calculated. The results show that the main magnetic moment of the system comes from Mn atoms. Of course, the interaction of Mn atoms with S atoms and the nearest neighbor O atoms also provides part of the magnetic moment. The magnetic moment of Mn atom is $1.52 \mu_B$, the magnetic moment of S atom is $-0.06 \mu_B$, and the magnetic moment of O atom ranges from 0 to $0.02 \mu_B$. Sn atoms basically have no contribution to the magnetic moment. The total magnetic moment is $1.5 \mu_B$. The integer magnetic moment shows that the doped SnO₂ is not a semi-metal. We will further discuss this issue through the density of states. Although O atom makes a small contribution to the magnetic moment, we can still find that O atom's contribution to the magnetic moment depends on its position. It is O atom, Mn's nearest neighbour, that produces part of the magnetic moment, while other O atoms make little contribution to the magnetic moment. As we all know, the physical and chemical properties of materials mainly depend on the electronic structure of the materials. Therefore, it is extremely important to study the electronic structure of doped SnO₂ samples. At the same time, in order to further study the origin of the magnetism of the system, we calculated the relevant electronic density of states diagram, as shown in Figure 2. It can be seen from the figure that the doped SnO₂ undergoes spin cleavage. In the total density of states, the number of spin-up electrons is more than the spin-down electrons. It can be found from the partial density of states that the magnetism of the system

is mainly caused by the spin splitting of Mn atoms. S atoms and O atoms also have a small contribution to the magnetic moment, while the Sn atom spin-up and spin-down electronic density of states is basically symmetrical, which makes little contribution to magnetism. It can be seen from the figure that there is no obvious exchange effect between Mn atoms and O atoms and S atoms. The magnetic moment of the system is mainly caused by the internal structure of the Mn atom itself.

Fig. 2. The DOS of Mn, S co-doping SnO₂.

In order to further explore its magnetic origin, let us consider the partial wave state density of each atom, as shown in Figure 3. The results show that O-2p and S-3p electrons have a small contribution to the magnetic moment, and most of the magnetic moment is provided by Mn-3d electrons. At the same time, we can also see that although it is relatively weak, there is still a coupling between the Mn-3d and S-3p orbitals near the Fermi level, and there is also an interaction between Mn-3d and O-2p. But as we have seen, the interaction is weak, and the main magnetic moment of the system may be due to the spin splitting of Mn-3d electrons.

Fig. 3. The PDOS of Mn, S co-doping SnO₂.

3.2 Dielectric function

The complex dielectric function is a physical quantity describing the propagation of electromagnetic waves in a medium, and it is also a bridge connecting the external electric field and the polarization of the medium. From the knowledge of physics, the polarization current can be divided into two parts. One part is generated by the real part of the dielectric, which lags the electric field by $\pi/2$. This part of the current does not lose energy, and the other

part is caused by the imaginary part of the dielectric. The current and the electric field are in phase, which will cause the absorption of electromagnetic waves, thereby consuming energy. We can even calculate that the energy absorbed by the medium per unit time is proportional to the imaginary part of the dielectric. Next, we will analyze the dielectric function of Mn and S co-doped SnO₂. The calculation results are shown in Figure 4.

The calculation results show that resonance excitation occurs at three points A, B and C, and the corresponding energy values of A, B and C are 7.349 eV, 8.485 eV and 9.859 eV respectively. These points have high energy loss due to the resonance excitation. Let's look at the dielectric imaginary part spectrum again. Its peak corresponds to the inter-band transition and will also cause significant energy loss. As shown in Figure 4, this system will undergo inter-band transition at D and E, and the corresponding energy values are 2.822 eV and 5.029 eV respectively.

Fig. 4. The dielectric function of Mn, S common doping SnO₂.

3.3 Complex refractive index

The dispersion relationship between refractive index and frequency, not only has important applications in various fields of optics, but even in particle physics. It is also used to study strong interactions, which shows its importance. The extinction coefficient also has important applications in many fields. After doping, we calculated the complex refractive index which was shown in Figure 5.

The calculation results show that 0-1.17 eV and 9.65-20 eV are the normal dispersion regions. At this time, the phase velocity of light decreases with the increase of frequency, and 1.17-9.65 eV is the abnormal dispersion region. At this time, the phase velocity of light was increased with frequency. It can even exceed the speed of light in vacuum. It is not the propagation speed of signals (or energy). It does not violate the theory of relativity. We can also see that at 3.16 eV and 6.01 eV, the extinction coefficient curve has two obvious peaks, and the peaks are 0.83 and 1.18 respectively. The results indicated that resonance absorption occurs here and the light wave energy corresponding to the natural frequency of the system also nearby.

Fig. 5. The complex refractive index curve of Mn, S common doping SnO₂.

4 Conclusion

(1) When Mn and S are doped into SnO₂, compared with pure SnO₂, the lattice constant is slightly increased, but the change is not big. It is indicating that the doping of Mn and S does not affect the crystal structure of SnO₂.

(2) In the Mn and S co-doped SnO₂ system, the phenomenon of spin splitting appears, and the system exhibits a ferromagnetic order. Regarding the origin of magnetism, we believe that the main magnetic moment of the system may be due to the spin splitting of Mn-3d electrons. At the same time, the coupling of the Mn-3d orbital and the S-3p orbital also makes a significant contribution to the magnetic properties of the system. One Mn atom provides a magnetic moment of 1.52 μ_B , and an S atom provides a magnetic moment of -0.06 μ_B . The adjacent O atoms also have a weak contribution to the magnetic moment, while Sn has almost no contribution to the magnetic moment. The total magnetic moment of the system is 1.5 μ_B , indicating that the doped system is not semi-metallic.

(3) The doping system in the 0-10 eV band is mainly anomalous dispersion, and the 10-20 eV band is normal dispersion; the absorption of light is also concentrated in the 0-10 eV band, and the 10-20 eV band is basically light No absorption.

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