Research Article

The Electronic Structures and Optical Properties of Electron Tuned Fe-Doped SnO_2 Materials

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By means of the full-potential linearized augmented plane-wave method (FP-LAPW), the electronic structures and optical properties of $\text{Sn}_{15}\text{FeO}_{32}$ with electron-injection are studied. The results show that Fe-doped SnO_2 materials are all direct transition semiconductors. The Fermi level goes into conduction band gradually and the band gap decreases with the increase of electron injection. The peaks of optical properties, such as the imaginary part of dielectric function and absorption spectra, change greatly at low energy. The absorption spectra exhibit blue shift, and the optical absorption edge increases, which are consistent with the change of the band gaps.

1. Introduction

The diluted magnetic semiconductors (DMS) have attracted a lot of experimental and theoretical attention [1–4] because their spin and charges can be manipulated, which will hereby induce many interestingly magnetic and magnetooptic characteristics. Though the magnetic and electronic properties in some typical DMS systems, such as SnO_2 , ZnO , and GaN , have been investigated extensively, many challenges to realize DMS materials for practical applications [5–7] still exist.

As a wide band-gap semiconductor, doped SnO_2 play a promising role in short-wavelength LED, gas sensor, and laser diode due to its large band gap (3.6 eV) and high exciton binding energy (130 meV) at the room temperature [8–10]. The electronic structures, magnetic, and optical properties of transition metal (Co, Cr, Mo, Eu, etc.) doped SnO_2 bulk semiconductors materials have been researched in theory and experiment [11–13]. As the important one of the family, the structures and optical properties of Fe-doped SnO_2 have also caused much attention [14–16]. Adhikari et al. [17] fabricated Fe-doped SnO_2 nanoparticles with a chemical coprecipitation method and studied their structures and magnetism. Kim et al. [18] studied the structure, magnetic and optical properties, and Hall effects of Co- and Fe-doped SnO_2 . When Fe doped SnO_2 , for charge balance, Fe ions must have the ionic

valence of Fe^{4+} without introducing any defects [19]. But Fe ions do not have 4+ oxidation state; hence, the holes are created. So the electronic injection is necessary to obtain the better performance of SnO_2 . It is well known that the injection of electrons into semiconductors is indispensable to realize spin-related devices, such as spin transistors [20]. The bleach in the absorption spectra by using size-dependent electron injection from excited CdSe quantum dots into TiO_2 nanoparticles is observed. It can be theoretically predicted using the first principles calculation, even if there are many difficulties such as the room temperature and external magnetic field in experiment [21, 22]. In this work, first-principles spin polarized calculations were used to explore the electron injection into Fe-doped SnO_2 , and its optical and magnetic properties were studied in order to understand the transition mechanism.

2. Computational Details

The first-principle calculations are performed using FP-LAPW as implemented in WIEN2k code [23, 24]. The exchange and correlation effects are treated with the generalized gradient approximations (GGA) [25, 26]. The parameter of $R_{\text{mt}}K_{\text{max}}$ is chosen to be seven (R_{mt} is the smallest muffin-tin radius in the unit cell and K_{max} is the cut-off for the plane

FIGURE 1: (Color online) The total DOS of the $\text{Sn}_{15}\text{FeO}_{32}$ supercell. The blue lines represent total DOS and the red lines represent Fe total DOS, respectively. (a) $x = 0$, (b) $x = 0.3$, (c) $x = 1.0$, and (d) $x = 1.5$.

wave). The cut-off energy required in the calculations of the solid state is 0.0001Ry. For k -space integration, a grid of $4 \times 3 \times 3k$ points in the first Brillouin zone is used. Atomic sphere radii of Sn, O, and Fe atoms are set to be 2.0, 1.8, and 2.0 a.u., respectively. The lattice parameters of SnO_2 crystals are consistent with the experimental values, which are $a = b = 0.4737$ nm, $c = 0.3186$ nm, and $\alpha = \beta = \gamma = 90^\circ$ [27].

All calculation models are constructed with $2 \times 2 \times 2$ supercell of SnO_2 , which contains 16 Sn atoms and 32 O atoms. In current work, only substitutional doping of Fe with Sn atoms is considered. Then, electron injection into $\text{Sn}_{15}\text{FeO}_{32}$ is taken with electron concentrations of $x = 0, 0.3, 0.5, 1.0, 1.2$, and 1.5 , respectively, and x is electron injection concentrations. The valence states for Sn, O, are Fe are $5s^25p^2$, $2s^22p^4$, and $3d^64s^2$, respectively.

3. Results and Discussion

3.1. Electronic Structure

3.1.1. Density of States (DOS). The calculated total DOS of the $\text{Sn}_{15}\text{FeO}_{32}$ supercell is shown in Figure 1. It can be seen that Fe substitutions into SnO_2 DMS induce exchange-split impurity states in the band gap, and the size of impurity states increases with the increase of injected electrons. When the concentration of injected electrons is less than 1.0, the material shows a half-metallic behavior with the majority

spin being semiconducting and the minority spin being metallic with sufficient unfilled states above the Fermi level. The 100% spin polarization carriers suggest that electron-injected Fe-doped SnO_2 can be used for spin injection where highly polarized spin current is desired. With the increase of the injected electrons, the conduction band moves to valence band gradually. Besides that, the DOS near the Fermi level reverses when the injected electron is 1.0. When the concentration of injected electrons is large than 1.0, the material shows a metallic behavior with both the majority spin and minority spin across the Fermi level.

The total and partial DOS of $\text{Sn}_{15}\text{FeO}_{32}$ supercell with electron-injection concentration $x = 0$ and 1.0 are presented in Figure 2, respectively. The coupling effect of Fe d, O p, and Sn p states can be found after Fe doping from Figure 2. The impurity states in the band gap are mostly composed of Fe 3d state hybridized with the O 2p states. The DOS (Figure 2(b)) indicates that the exchange-split Fe 3d states strongly hybridize with the O 2p states at the top of the valence band, which is partly spin-polarized. When electron-injection concentration is 1.0, the partial DOS of Fe atom is greatly changed, especially in the Fermi level. The lowermost valence bands largely derive from Fe 3d, O 2p, and Sn 5p state when the band ranges from -6.0 to -3.5 eV. The O 2p state and Fe 3d state are formed when the bands are between -3.5 and -0.7 eV. The states derive from Fe 3d when the bands are between -0.7 and 0.3 eV. However, the states derive from Fe

FIGURE 2: (Color online) Total DOS plots and partial DOS plots of the $\text{Sn}_{15}\text{FeO}_{32}$ supercell with electron-injection (1) $x = 0$ and (2) $x = 1.0$.

3d and O 2p when electron-injection concentration is 1.0, and Fe 3d turns to down from spin up, indicating that particles reverse has happened. When the bands are in the range from 0.3 to 2.6 eV, the states mainly derive from Fe 3d. When the bands locate in the range from 2.6 to 6.0 eV, the states mainly derive from Sn 5p.

3.1.2. Band Structure. The band structure of $\text{Sn}_{15}\text{FeO}_{32}$ supercell is shown in Figure 3, when $x = 0.5$. At the Fermi level, occupied and not occupied electrons exist when spin down and up, respectively. Figure 4 shows the band structures of spin-up $\text{Sn}_{15}\text{FeO}_{32}$ with the concentration of inject electrons to be 1.0 and 1.5. Furthermore the band gaps become narrower and narrower until zero with the increase of the injected electrons, indicating the excellent conductivity. Each band

structure displays a direct band gap at the highly symmetric G point as well as in pure SnO_2 , as shown in [28].

3.2. Optical Properties. It is well known that the interaction of a photon with the electrons can be described according to time-dependent perturbations of the ground-state electronic states, and the optical transitions between occupied and unoccupied states are caused by the electric field of the photon. More importantly, solid dielectric function reflects the information between energy band structure and optical spectral lines and can characterize the physical properties of materials. The formula of dielectric function is defined by

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega), \quad (1)$$

where $\varepsilon_1(\omega)$ is the real part of the function, while $\varepsilon_2(\omega)$ is the imaginary part.

FIGURE 3: Band structures for supercell: $\text{Sn}_{15}\text{FeO}_{32}$. (a) $x = 0.5$ when spin up and (b) $x = 0.5$ when spin down.

FIGURE 4: Band structures for supercell: $\text{Sn}_{15}\text{FeO}_{32}$. (a) $x = 1.0$ and (b) $x = 1.5$.

The real part $\epsilon_1(\omega)$ of the dielectric function can be evaluated from the imaginary part $\epsilon_2(\omega)$ by the Kramer-Kronig relationship, while the imaginary part $\epsilon_2(\omega)$ has the following expression [29]:

$$\epsilon_2(\omega) = \frac{4\pi^2}{m^2\omega^2} \sum_{V,C} \int_{\text{BZ}} d^3k \frac{2}{2\pi} |e \cdot M_{cv}(K)|^2 \times \delta[E_C(k) - E_V(k) - \hbar\omega]. \quad (2)$$

FIGURE 5: The imaginary part of dielectric function $\varepsilon_2(\omega)$ of $\text{Sn}_{15}\text{FeO}_{32}$ with electron-injection.

Among this, $\hbar = h/2\pi$, m is the mass of free electrons, e is the charge of free electrons, ω is the frequency of incident photons, C represents the conduction band, V represents valence band, BZ represents the first Brillouin Zone, and K is the reciprocal vector.

Figure 5 shows the imaginary spectra of optical dielectric function $\varepsilon_2(\omega)$, with the number of ions of 0, 0.3, 0.5, 1.0, 1.2, and 1.5. There are three main dielectric peaks ranging from 7.0 to 14.0 eV. The first peak at about 7.1 eV should mainly be caused by the transition between O 2p state in the highest valence band and Sn 5s in the lowest conduction band. The second peak located at about 9.8 eV mainly derives from the transition from O 2p to Sn 5p state, which is reflected by the DOS. The peak at 14.0 eV can be attributed to the combination of the transition between O 2s and Sn 5s and that between Fe 3d and Sn 5p. At the same time, there are some unapparent folded peaks, and they could be attributed to multilevels direct or indirect transition. From 0 to 5.0 eV, the peaks changed greatly, which are in consistency with the DOS in Figure 1.

Figure 6 shows the absorption spectra with the number of ions of 0, 0.3, 0.5, 1, 1.2, and 1.5. In the imaginary spectra of optical dielectric function, three main dielectric peaks exist ranging from 7.2 to 12.0 eV, which have no significant differences between various electron-injections, and are in consistency with the dielectric function in Figure 6. As the electron concentrations increase, the overall curves move to the high energy, that is the blue-shift. From 0 to 5.0 eV, the peaks changed greatly, the results are consistent with the Ref 30 of Fe-doped TiO_2 . The spectra become smooth gradually, and the float/drift of the intensities is not apparent, indicating that such optical and electronic devices can work relatively stable.

4. Conclusions

In summary, the band structure, the total and partial DOS, and the optical properties of $\text{Sn}_{15}\text{FeO}_{32}$ with electron

FIGURE 6: Absorption spectra of $\text{Sn}_{15}\text{FeO}_{32}$ with electron-injection.

injection have been investigated by the FP-LAPW method. With the increase of the injected electrons, the conduction band moves to valence band gradually. The SnO_2 material shows half-metallic properties when the injected electron is less than 1.0. There exists strong coupling interaction between Fe atom and O atom. For the optical properties (the imaginary part of dielectric function, absorption, and reflection), we found that the peaks changed greatly at low energy, the blue shift occurred, and the optical absorption edge increased.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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