Enhancement of absorption and conductivity of CdS in the infrared range with Cu dopant

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Abstract

The Cu dopant effect on the optical properties of zinc-blende phase CdS in the infrared range has been investigated, based on calculations using the first principle density functional theory with Hubbard U on site correction. Four concentrations of Cu dopant are considered. The results show that the Cu-doped CdS demonstrates a significantly enhanced behavior of absorption and conductivity in the infrared range, implicating that it could be a promising candidate for the infrared switch materials. The mechanism of the enhancement has also been explored. It is found that the Cu dopant induces a hole state above the Fermi energy level (E_F) of CdS, and provides a possible intraband transition with about 0.7 eV energy difference, which is responsible for the enhanced absorption of CdS in the infrared range.

Keywords: optical properties; infrared absorption; intraband transition; dopant

1. Introduction

Semiconductors have been paid much attention due to their potential use as photoconductors and in fabricating optical detectors, light sources and optoelectronic devices [1-3]. CdS as a kind of typical II-IV semiconductor compounds is a kind of good photoelectric material because it has the excellent photoelectric conversion characteristic and luminous performance over the ultraviolet range. The pristine and impurity CdS have been

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extensively studied in both theoretical and experimental works [4-11]. Cu-doped CdS quantum dots as a fluorescence imaging probes in living cells and emitting near-infrared light have been experimentally investigated by Zhang *et. al* [12]. They successfully synthesized a water soluble Cu-doped CdS quantum dot (Cu @ CdS d-dots) with an emission wavelength of 722 nm using a fast and facile hydrothermal method. They successfully gained the fluorescence image of living HeLa cells was via labeling with the near-infrared emission Cu:CdS d-dots in aqueous solution directly under ultraviolet irradiation. They also presented a qualitative description of the mechanism for near-infrared emission. However, the mechanism for the enhancement of absorption in infrared range CdS by the Cu dopant has not been elaborated.

The pristine CdS is a direct band gap semiconductor material, and the band gap is 2.42eV [13], which is relatively smaller than some other compound semiconductor (3.26eV for TiO₂ [14] and 3.37eV for ZnO [15]). CdS can be hexagonal wurtzite or zinc blende structure. The optical properties of the both are necessary when one prepares the Cu-doped CdS materials. The pristine CdS has a large absorption coefficient in the visible light range and can be enhanced by the dopant. For example, Han *et.al* [16] reported that the absorption coefficient in the visible light range of CdS can be significantly enhanced by Fe dopant. Recently, the magnetic properties and optical properties of the hexagonal wurtzite structure of CdS doped with Cu has been theoretically investigated [10]. The absorption enhancement in the infrared range is also found. Unfortunately, the mechanism remains unclear. On the other hand, we failed to find the report on the optical properties of the zinc blende structure of CdS doping Cu. Therefore, we perform investigations on the Cu doping zinc blende structure of CdS based on the first principle calculations. The mechanism of the enhancement of

absorption and conductivity in the infrared range has been explained.

2. Models and calculation method

As the structure shown in Fig 1, we have built a $2 \times 2 \times 2$ supercell firstly, using the conventional cell of the pristine zinc-blende phase CdS. As a result, the supercell includes 64 atoms. The initial cell parameters of the primitive pristine CdS are taken from the experimental values, i.e., $a=b=c=5.830\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$. [17] Each Cd atom is located in the center of the tetrahedron composed of four S atoms. The considered Cu-doped ways are to replace a Cd atom in the supercell with a Cu atom at roughly symmetrical positions. As shown in Fig.1 (b), the numbers of the doped Cu atoms are 1, 3, 5, and 7, which correspond to 1.42wt. %, 4.49wt. %, 7.90wt. %, and 11.70 wt. % of the concentrations, respectively. Hereafter, they are represented by 1Cu@CdS, 3Cu@CdS, 5Cu@CdS, and 7Cu@CdS. For each concentration, some different doped positions are possible. In the present, we mainly consider the symmetry arrangement of the doped Cu atom which results in the smallest change of the supercell geometry of CdS.

Based on density functional theory, all the calculations are carried out by using the functional of Perdew, Burke and Ernzerhof [18, 19] with the general gradient approximations and Hubbard U on-site correction (GGA + U). [20] The valence electron electronic configurations are $4d^{10}5s^2$ for Cd, $3s^23p^4$ for S and $3d^{10}4s^1$ for Cu, respectively. The values of Hubbard U are 4.0 eV for 3d electrons of Cd and Cu, and 2.0 eV for 2p electrons of S according to the values used in the literature. [4, 15] In order to obtain more reliable results, the norm-conserving pseudopotential is used in all the calculations of the electronic and optical properties, although the computational time consumption will significantly increase.

Both the lattice parameters and the positions of all atoms for the supercells of the

pristine and the doped CdS are fully relaxed before calculating the electronic and optical properties. The number of conduction bands, cutoff energy, convergence in energy, force stress, and displacement are set as 20, 880eV, 2.0×10^{-5} eV, 0.05 eV/Å, 0.1 GPa and 0.002 Å, respectively. Total 5 high symmetry k points are used in Brillouin zone.

3. Results and discussion

3.1 Geometrical structure and electronic properties

The optimized lattice parameters of the pristine and doped zinc-blende phase CdS are listed in Table 1. The present result for the pristine CdS is in agreement with the experimental and other theoretical value although a little larger than them. The present lattice parameter of 6.0 Å is very close to 5.976 Å of Han *et al* [16]. The little difference should be resulted from the different pseudopotential because their optimization calculations are carried out using GGA+U method with ultrasoft pseudopotential. Ma *et al* [21] obtained 5.85 Å using GGA with the projector augmented wave (PAW) potentials, [22] which is a little better in comparison with the experimental 5.83 Å [17]. The optimized lattice parameters of the Cu-doped CdS are smaller than that of pristine CdS and they always decrease along with the increase of the doped concentrations. The same tendency has been shown for average bond lengths of $d_{\text{Cd-S}}$ and $d_{\text{Cu-S}}$. That is, the average of Cd–S band length becomes smaller when doping with Cu atoms. These changes can be understood via the fact that the ionic radius of Cu atom is smaller than that of Cd atom.

To examine the doping possibility of Cu and identify the stable dopant position, we calculate the formation energy of the Cu dopant in the CdS defined by

$$E_{\text{form}} = E(n\text{Cu}@ \text{CdS}) - E(\text{CdS}) + n_{\text{S}}\mu_{\text{S}} + n_{\text{Cd}}\mu_{\text{Cd}} - n_{\text{Cu}}\mu_{\text{Cu}}$$

Where E_{form} is the formation energy. $E(n\text{Cu}@ \text{CdS})$ is the total energy of the supercell

with n Cd atoms replaced by Cu atoms and $E(\text{CdS})$ is the corresponding energy in the bulk structure. n is the number of ions (Cd, S, or Cu) exchanged between a perfect cell and its corresponding reservoir to form a defect, and μ is the chemical potential of Cu, S, or Cd and calculated by the same theoretical level as that of the total energy calculation. The calculated formation energies are presented in Table 1. The E_{form} for the 1Cu and 3Cu atoms doped CdS are 1.21 and 3.92 eV, respectively. They are larger than 0.74 and 1.16 eV [10] for the corresponding case of Cu-doped wurtzite phase CdS, which means that to dope Cu in the zinc-blende phase CdS is more difficult. The larger E_{form} also implies that the Cu-doped zinc-blende phase CdS is less stable compared to the Cu-doped wurtzite phase CdS. However, the moderate formation energies (smaller than 10.0 eV) for the doped atoms are acceptable. Moreover, the results in the following section will demonstrate that 4.49 wt. % is large enough to obtain the novel optical properties. It is 3.915 eV of formation energy for the doped structure, which should be not too high for experimental synthesis.

The present 2.061 eV of band gap for the pristine CdS is close to that of Han *et al.* [16]. The band gaps decrease obviously when CdS is doped with Cu atoms. However, the reduction has not shown an obvious quantitative relationship to the Cu-doped concentrations. To understand the Cu-doped effect on the band gap, we have calculated the total density of state (DOS) and presented them in Fig. 2. To demonstrate the band energy gap clearly, we have also presented an enlarged version for the part near the borders of the prohibitive band in Fig. 2 (b). Carefully examining the figure, one can find that the change of the minimum of the conductive band is not very large, and the reduction of the band gap is resulted in mainly by the hole state of 0.25-0.5 eV above E_F . Therefore, the obvious reduction of the band gap has not explicitly effected on the interband transition, and the absorption in the visible light

range shows a little change, more details are presented in the next section.

3.2 Dielectric function and optical properties

In order to calculate the optical property of CdS, we firstly calculate the complex dielectric function. The results of the real part $\epsilon_1(\omega)$ and imaginary part $\epsilon_2(\omega)$ of the complex dielectric function are presented in Fig. 3. One can find in the figure that both $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are very small for the pristine CdS and 1Cu@CdS in the lower energy range, but significantly enhanced for the heavier Cu-doped CdS, which implies that the dopant concentrations play obviously on the dielectric functions. Comparing the curves of the dielectric functions with the total DOS in Fig. 2, one can find that the large $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ in the range below 0.5 eV of energy is not from the transition between the valence band and conduct band but from the transition between the valence band and the hole state above the E_F , which is similar to the case of F-doped γ -Si₃N₄. [23]

Based on the complex dielectric function, the absorption of the pristine and doped CdS are determined. The results are presented in Fig. 4. To demonstrate the change of absorption for the infrared range clearly, we also plot the absorption vs the wavelength of light in Fig. 4(b). The absorption is not significantly changed in the visible light range and not been changed in the ultraviolet range although a little decrease is observed along with the increase of the Cu dopant concentration. Fig. 4(b) shows that almost no absorption in the infrared range is shown for the pristine CdS and a little for the 1Cu@CdS. However, the obviously enhanced absorptions in the infrared range are found for the 3Cu@CdS, 5Cu@CdS and 7Cu@CdS, respectively. It implies that the Cu dopant can significantly enhance the absorption in the infrared range if the doping concentration is large enough. The figure also shows that the absorption peaks have a little difference for the three heavier doping

concentrations, which means that the 3Cu@CdS (4.49 wt % Cu) is enough to obtain the infrared enhancement of the absorption, and heavier doping concentration is likely unnecessary for this effect.

We also calculated the photoconductivity for the Cu-doped CdS. The results in Fig.5 show that the infrared wavelength range alternating current optical conductivity, considered as the photoconductivity here, is significantly enhanced in the infrared range, which implies that the conductivity will increase when the infrared light is thrown on the Cu-doped CdS. The obvious enhancement of both absorption and photoconductivity makes it a promising candidate as a switching material in the infrared range.

Zhang *et al* [12] have reported that the Cu-doped CdS quantum dots can emit light with a wavelength of 722 nm and the wavelength decrease along with the ratio of Cu. The present E_g s in table 1 corresponds to the emission wavelength of 793, 788, 718, and 723 nm, which show a similar tendency as that of Cu-doped CdS quantum dots.

3.3 Mechanism of the enhancement of absorption

There are many reports on the absorption of semiconductor enhanced with a dopant in the visible range, while the enhanced absorption in the infrared range is not usually observed. To understand the mechanism of the infrared enhancement of the absorption for CdS doped with Cu, we analyze the DOS and the projected density of state (PDOS) for both the pristine and the doped CdS. The results are demonstrated in Fig. 6. The total DOS for the pristine and doped CdS have been shown in Fig. 2 (a). It is demonstrated in the figure that the dopant Cu induces a hole state above the E_F . The first peaks of DOS for the doped CdS below the E_F are located at about from -0.2 to -0.4 eV. There is the infrared absorption if they transit to the hole state. Moreover, the peak of the hole state is weak for 1Cu@CdS but stronger for the

heavier doped concentrations, which induce the more significant enhancement absorption of the heavier Cu-doped CdS in comparison of that of the 1Cu@CdS.

We present the PDOS for the both cases of pristine and Cu-doped CdS in Fig. 6 to demonstrate the doping effect of Cu clearly. From Fig. 6(a) for the PDOS of the pristine CdS, one can find that both the highest energy levels of the d partial DOS of Cd atom and the p partial DOS of S atoms cross the E_F , but no peak is located above E_F , which means that there is no hole state for the pristine CdS and intraband transition is impossible. Fig. 6(b)-6(e) show that the doped Cu directly provides a peak of d partial DOS above E_F for the 1Cu@CdS case, which results in a weak absorption in the infrared range. Moreover, for the heavier doped cases, the doped Cu also induces a peak of the p partial DOS for S atom above E_F . Adding d partial DOS of the Cu atom and the p partial DOS of S together, one can obtain a higher peak of DOS, which provides a stronger intraband transition. Therefore, both the intraband transition between the $3d$ states of Cu and the transition between the $2p$ states of S contribute the infrared absorption of the doped CdS. It is responsible for the significant enhancement of the infrared absorption of the Cu-doped CdS. The figure also shows that the Cd has little contribution to the hole state peaks above E_F , and the concentration of the doped Cu impact a little change on the peaks, either. It implies that the 4.49 wt. % is enough to significantly enhance the infrared absorption and heavier concentration is unnecessary.

The enhancement of the photoconductivity is also understood via the similar intraband transition. When the infrared light is thrown on the Cu-doped CdS, some electrons will enter the hole state and increases the movable electron because intraband transition. These electron above the E_F can be used charge carriers, which is responsible for the increase of the conductivity. However, the intraband transition does not happen when the energy of the

projected light become larger than the energy difference between the valence band and the hole state. Therefore, the photoconductivity in the range of the visible light obviously decreases. It increases again in the ultraviolet region because the interband absorption is strong in the range. The Cu-doped CdS can be used as infrared switch material because the conductivity occurs when the infrared light is thrown on it.

4. Conclusion

The absorption and conductivity in the infrared range for the Cu-doped zinc blende CdS is examined with the first principles calculations. The significant enhancement of the both has been observed, implicating that the Cu-doped CdS could be used as an infrared switch material. The infrared absorption enhancement results from the intraband transition between the valence band and the hole state. The Cu dopant contributes a hole state on the E_F with its $3d$ state, and induces the $2p$ state of S atom lifting and strengthening the hole state when the dopant concentration is larger than 4.49 wt. %. The heavier concentrations impact only a little increase the enhancement of the infrared absorption, which implies that the 4.49 wt. % is large enough to obtain the satisfactory infrared absorption. Considering that both the Cu-doped hexagonal wurtzite reported in the literature [9] and the zinc blende in the present investigations can demonstrate obvious infrared absorption, the Cu-doped zinc-blende and wurtzite CdS should be a promising candidate for the infrared material.

Acknowledgments

This work was supported by the National Science Foundation of China (NSFC) under Grant Nos. NSFC-11574125 and NSFC-11374132, as well as the Taishan Scholars project of Shandong Province (ts201511055).

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Figure captions

Fig.1. The structure of CdS ($2\times 2\times 2$) supercell. (a) Intrinsic CdS. (b) Doped $\text{Cd}_{32-x}\text{S}_{32-x}\text{Cu}_x$. The yellow, red and green balls represent S, Cu and Cd, respectively. The atom with a number represents the position of the substitute Cu atoms.

Fig.2 The total DOS of the intrinsic and doped CdS. (a) The total DOS; (b) The total DOS near the prohibitive energy gap to demonstrate the energy gaps.

Fig.3 The complex dielectric function of the doped CdS. (a) the imaginary part, (b) the real part.

Fig.4 The absorption coefficient. The abscissa axis is in eV for (a) and in nm for (b).

Fig.5 The real part of the alternating current conductivity of the intrinsic and doped CdS.

Fig.6 The PDOS of the intrinsic and doped CdS.

Table 1 The geometrical structures and electric properties of the intrinsic and Cu-doped zinc-blende phase CdS. (d_L represents the lattice parameter, and $d_{\text{Cd-S}}$ and $d_{\text{Cu-S}}$ are the average bond length in Å. E_g and E_{form} are the band gap and formation energy in eV)

Cu (wt. %)	d_L	$d_{\text{Cd-S}}$	$d_{\text{Cu-S}}$	E_g	E_{form}
intrinsic	6.000 5.976[16] 5.83 [17] 5.85 [21]	2.601 2.525[13] 2.587[16]		2.061 2.42 [13] 2.056 [16]	
1.42	5.945	2.600	2.402	1.562	1.21 0.74*
4.49	5.933	2.596	2.403	1.573	3.92 1.16*
7.90	5.879	2.593	2.382	1.726	6.53
11.70	5.862	2.589	2.377	1.714	9.307

* for Cu-doped wurtzite phase CdS, from Ref. [10].

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