Study on the Electronic Structures of ZnS and Ag-doped ZnS from Density Functional Theory

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Abstract: The band structures and electronic structures of pristine and Ag-doped zinc blende ZnS were calculated with the ab-initio ultra-soft pseudopotential plane wave approximation method based on density functional theory (DFT). The results show that Ag-doping narrows the band gap of ZnS and the acceptor impurity level is introduced by importing impurity Ag. It is pointed out that the acceptor level is hybridization due to the overlapping of the Ag-4d and S-3p. By analysis of Mulliken populations, Zn-S bond has strong covalence in ZnS and the covalence of bond Ag-S is weakest after Ag-doped.

Introduction

Over the past decades, Zinc sulfide (ZnS) with a direct band gap of 3.68eV for the zinc-blende(ZB) structure at room temperature[1] has been attracted more attentions because of its potential applications in nano-optoelectronic and environmental remedy industries such as light emission diodes (LED), nano-sensors, dye-sensitized solar cells and photocatalysts[2-7]. However, the wavelength range of which pure ZnS materials can stimulate is limited, and pure ZnS material has some flaws which hinder it from further applied research. Hence, an effort to either modulate the band structure of ZnS to meet the special functions is being pursued. By doping different kinds of elements, the semiconductor material band gap can be reduced and the electronic structure can be improved, which helps to enhance the response of the visible light and the photocatalytic activity[8].

The study found that ZnS is a kind of preferred substrate material to be doped with transition metal elements or rare earth elements as active particles, which provides convenient conditions for the modification of ZnS properties by doping. In chemical reactions, d-state electrons of transition metal atoms are all involved in the formation of chemical bonds. That means the d-state electrons can show a variety of oxidation properties. Because of the bonding empty d-state of the transiting metal, many ligands are easy to form stable coordination compound. In this mechanism the transiting metal shows a higher catalytic activity, especially the transition metal atoms doped semiconductor materials which have been the subject of much public concern. ZnS doped with transition metals Ag were investigated in detail.

The electronic structure of semiconductor material determines its physical properties. Based on the first-principles methods of density functional theory (DFT), we conducted analog calculations on the electronic structures of ZnS and Ag-doped ZnS. The results show that Ag-doping narrows the band gap of ZnS and the acceptor impurity level is introduced by importing impurity Ag**.**

Theoretical method and computational details

Sphalerite ZnS was adopted in the calculation. We constructed 2×1×1 ZnS supercell model and doped ones (shown in the Fig.1). At a quarter of unit cell body diagonals were S atoms, likewise, at the eight top corners and six center of face were Zn atoms, each unit cell contained 4 Zn atoms and 4 S atoms. Doped Ag atoms substituted respectively Zn atoms at (0.5, 0.5, 0.5) in the unit cell, as shown in Fig.1. The calculations were performed using CASTEP code[9] based on first-principles DFT. The external

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potential of the valence electron in the system took ultrasoft pseudopotential, the exchange and correlation interactions were modeled using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function[10]. The energy cutoff (Ecut) of planewave functions was set to 350.0 eV. All atomic positions in the ZnS supercell had been relaxed according to the total energy and force using the BFGS scheme[11], based on the cell optimization criterion (RMS force of 0.01 eV/Å, stress of 0.02 GPa, and displacement of 5.0×10^{-4} Å). The calculation of total energy and electronic structures was followed by cell optimization with SCF tolerance of 5.0×10^{-7}eV/atom. The k mesh points of 3×6×6 under the Monkhorst-Pack programme[12] were used in the calculation for integrations over the Brillouin zones of ZnS and Ag doped-ZnS.

Atoms of the same species were completely equivalent in the ZnS crystal lattice. While the same species atoms which located different place had different population after importing impurity. So we had to classify them. Fig.1 showed that the blue atom was Ag, the gray atoms were Zn and the yellow were S. S atoms were classified two sorts: Ⅰ sort atoms were signed 1,4,6,7 in the picture and Ⅱ sort atoms connected with Ag directly were signed 2、3、5、8. Zn atoms were sorted four: Atoms marked 1 was Ⅰ sort, Ⅱ sort were marked with 2，Ⅲ sort were marked with 5，and the others（signed 3、4、6、7 in the picture）were Ⅳ sort.

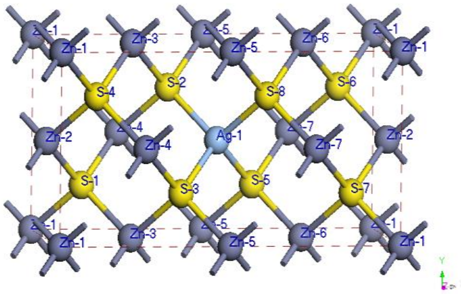


Fig.1. Structure for Ag-doped ZnS (2×1×1) supercell

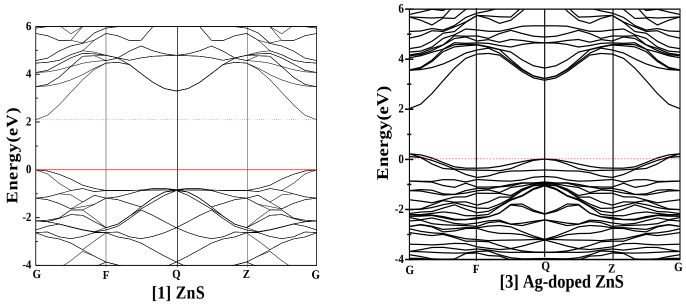


Fig. 2.The band structure of intrinsic system and doped ZnS

Results and Discussion

Structural optimization: To assess the accuracy of our computation method, we performed a series of calculations for cell optimization. The equilibrium lattice constants are a=b=c=0.54447 nm after optimization, which are in good agreement with experimental results (a=b=c=0.54093 nm) [13].

Electronic structure: Band structures of pristine ZnS and Ag-doped ZnS were presented in Fig.2. Zero of the band structure in Fig.2 was Fermi energy level. As illustrated in Fig.2-[1], the calculation shows a direct band gap of 2.097eV at the high symmetric G-point in the Brillouin zone for pristine ZnS, which is lower than the experiment value of 3.68eV. The bottom of conduction band and top of valence band both locate at G point, which is the representative characteristic for direct transition semiconductor. The band gap underestimation of DFT always exists as the result of the well-known limitation of predicting accurate energy band properties[14]. For Ag-doped ZnS, the calculated band gap value has a slight decrease compared with pristine ZnS (shown in Fig.2-[2]). Some levels pass through the Fermi level $\boldsymbol{E_f}$**,** indicating that Ag doped in ZnS acts as the acceptor impurity. The narrow band gap and the acceptor states in the gap are beneficial for improving the visible-light absorption and photocatalysis.

The density of states (DOS) and partial density of states (PDOS) of ZnS and Ag-doped ZnS systems were shown in Fig.3. Mulliken population of pure ZnS and Ag-doped ZnS were shown in Table1. to Table 3.

As shown in Fig.3[1], conduction bands mainly dominated by the valence electrons of Zn(4s,4p) and S(3p) orbits in the pure ZnS system mainly locate in the 4.0 to 10.0 eV energy range. A significant charge transfer from Zn(4s) to S(3p) orbits shown in Table 1 and an overlap between the Zn(4s) and S(3p) valence electrons depicted in Figure 3[1] reveal not only covalent bonding but also ionic bonding between the FNN(first nearest neighbor) Zn-S in pure ZnS. Valence bands in pure ZnS are mainly combined by two part, that, top valence bands (4.9 to 0 eV) and bottom valence bands (6.8 to 4.9 eV), as illustrated in Fig.3[1]. It is worth noting that the top valence bands and bottom valence bands are mainly contributed by S(3p) and Zn(3d) orbits, respectively. In addition, the Zn(4s)-S(3p) hybridization at 4.3eV between the FNN Zn-S is observed.

Compared with pure ZnS, the total DOS and partial DOS of Ag-doped ZnS in Fig.3[2] show that after importing Ag at the side of top of valence band there are redundant carrier-cavity pairs that induced an acceptor band near the Fermi level.

Table 1. Mulliken population of pure ZnS system

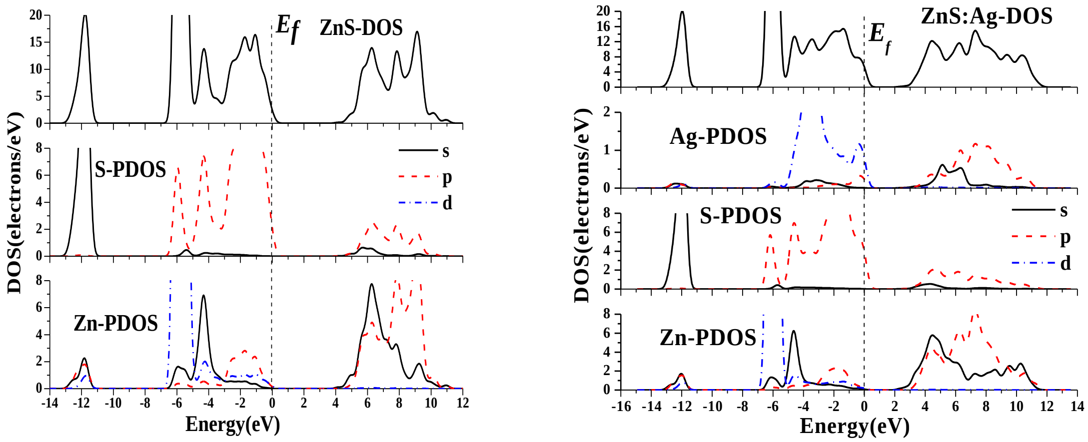
Species	s	p	d	f	Total	Charge(e)	Bond	S-Zn
S	1.82	4.65	0.00	0.00	6.47	-0.47	population	0.49
Zn	0.56	0.99	9.98	0.00	11.53	0.47	Bond length(Å)	2.360

Table 2. Mulliken population of Zn And S of Ag-doped ZnS (atomic population)

Species	number	s	p	d	f	Total	charge（e）
S	(1、4、6、7) Ⅰ	1.82	4.64	0.00	0.00	6.46	-0.46
	(2、3、5、8) Ⅱ	1.83	4.60	0.00	0.00	6.43	-0.43
Ag	Ⅰ	0.66	0.59	9.78	0.00	11.02	-0.02
Zn	(1) Ⅰ	0.55	0.96	9.98	0.00	11.49	0.51
	(2) Ⅱ	0.56	0.98	998	0.00	11.51	0.49
	(5)Ⅲ	0.51	1.00	9.97	0.00	11.48	0.52
	(3、4、6、7)Ⅳ	0.52	0.99	9.97	0.00	11.48	0.52

Table 3. Mulliken population of Ag-doped ZnS (bond population)

Bond	S Ⅰ -Zn Ⅰ	S Ⅰ -Zn Ⅱ	S Ⅰ -ZnⅣ	S Ⅱ -Zn Ⅲ	S Ⅱ -ZnⅣ	S Ⅱ -Ag
population	0.48	0.50	0.44	0.47	0.51	0.37
Bond length(Å)	2.3654	2.3451	2.3676	2.3583	2.3435	2.4972



[1] ZnS **[2] Ag-doped ZnS**

Fig.3 Calculated total and partial DOS of ZnS and Ag-doped ZnS

There are high activity 4d state electrons in transition metal Ag. As shown in Fig.3, the density of states (DOS) for Zn in the pristine ZnS are almost the same as Ag-doped ZnS, whereas, the DOS for S, especially the partial density of states (PDOS) for S 3p state electrons， show significant changes. It is the doped Ag impurity nearest to those S atoms that shows a strong influence on the S atoms. Apparently, the DOS for doped systems illustrate obvious changes compared with pristine ZnS in the valence band (VB) top range. The impurity levels found on the VB top are mainly originated from the Ag-4d states hybridized with the S-3p states. These strong hybridization energy levels compose weakened localized type or dispersion type DOS which suggests high mobility of photogenerated carrier in the doped systems, which is mainly attributed to the contribution of 4d state electrons of transition metal Ag.

The overlapped population is used to estimate that the bond is covalent or ionic. The bond with high overlapped population is covalent bond and the bond with low overlapped population has strong ionicity. Moreover the bigger population is, the stronger valence of bond is. The results in Table 2-3 show that the system of Ag-doped ZnS included not only covalent bonding but also ionic bonding. The covalency of SⅡ-Ag bonds is weakest and population is smallest which made electrons of S close to Zn. So population of SⅡ-ZnⅣ is biggest, its covalency is strongest and its bond lengths are shortest. The bond lengths have low different values in the sort of SⅠ-ZnⅠ bond. This was because relative location of atoms made a tiny shift after importing impurity. But it did not influence a lot the analysis of state density.

Conclusions

The band structures, electronic structures and Mulliken populations of ZnS and Ag-doped ZnS have been computed by means of plane wave ultra-soft pseudopotential method with generalized gradient approximation which is based on the density functional theory. The thermal band gap of ZnS becomes small after Ag-doped. In the analysis of electronic structures, an acceptor band is induced because of doping Ag. It is pointed out that the acceptor level is hybridization due to the overlapping of the Ag-4d and S-3p. By analysis of the Mulliken populations, the systems of ZnS and Ag-doped ZnS include not only covalent bonding but also ionic bonding. After doping Ag, Zn-S bonds have strong covalence and the covalence of bond Ag-S is weakest after Ag-doped since its bond length is longest.

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