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The effect of electronic orbital interactions on p-type doping tendency in ZnO series: First-principles calculations*

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The electronic structures and optical properties of B3 ZnO series of $Zn_4X_{4-y}M_y$(X =O, S, Se or Te; $M = N$, Sb, Cl or I; $y = 0$ or 1) are studied by first-principles calculations using a pseudopotential plane-wave method. The results show that Zn d-X p orbital interactions play an important role in the p-type doping tendency in zinc-based II-VI semiconductors. In ZnX, with increasing atomic number of X, Zn d-X p orbital interactions decrease and Zn s-X p orbital interactions increase. Additionally, substituting group-V elements for X will reduce the Zn d-X p orbital interactions while substituting group-VII elements for X will increase the Zn d-X p orbital interactions. The results also show that group-V-doped ZnX and group-VII-doped ZnX exhibit different optical behaviours due to their different orbital interaction effects.

Keywords: electronic structures, optical properties, pseudopotential plane-wave method, p-type doping tendency
PACC: 7125, 7280E, 7115H, 7890

1. Introduction

Zinc-based II-VI wide-band-gap semiconductors have been of great interest since at least twenty years ago for their assorted physical properties such as electro-optical, acousto-optical, and luminescence characteristics. However, the production of zinc-based II-VI devices has been hindered by difficulties in fabricating p-(or n-)type materials. ZnO, ZnS, and ZnSe are natural n-type semiconductors, which are easy to be doped as n-type semiconductors but difficult to be doped as p-type ones. On the contrary, ZnTe is a natural p-type semiconductor and is easy to be doped as p-type semiconductors but difficult to be doped as n-type ones.[1] Several mechanisms leading to the doping difficulty such as low solubility,[2] compensation by low-energy native defects,[3] and structural bistability are known as acceptor-excited (AX) center[4] in doped natural n-type materials and donor-excited (DX) center[5] in doped natural p-type materials. Researchers have been trying to find a way to break the bottleneck. For example, a latest work has reported a co-doping method by theoretical calculations.[6] But so far few experiments approve this prediction. This makes the difficulties hang in the balance. The doping properties actually behave via the electronic interactions between orbitals so that a detailed investigation of orbital interactions is necessary to understand the doping properties of ZnX (X =O, S, Se, or Te).

Thus in the present work, we make a detailed study on the electronic orbital interactions of ZnX (X=O, S, Se or Te) to address the above problem. For the most active electrons of Zn are s electrons, and those of X are s and p electrons, in which p orbital is unfully-filled, the electronic interaction in ZnX mainly comes from Zn s and X p. However, Zn d electrons also play an important role in the electronic properties of ZnXs.[7,8] Hence the interactions between Zn s (d) and X p are considered together in this work. In ZnXs, group-VII elements Cl and I as substitutional element for X can be used as n-type dopants,[9] and group-V elements N and Sb as substitutional element for X can be used as p-type ones.[4] As the conductive characteristics that change from ZnO (n-type) to ZnTe (p-type) are similar to those from ZnX to Zn_4X_3M (M=N or Sb) and opposite to those from

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ZnX to Zn_4X_3M (M=Cl or I), the electronic orbital interactions between ZnX and Zn_4X_3M are comparable. Thereby we also probe the electronic orbital interactions in doped systems Zn_4X_3M(X=O, S, Se or Te; M=N, Sb, Cl or I). Since ZnXs have drawn considerable interest mainly due to their potential applications in optoelectronic devices, the optical spectra have also been investigated. This paper is organized in the following way: Section 2 describes the calculation in detail. Section 3 presents the results and discussions. A brief summary is given in Section 4.

2. Computational method

All the calculations are performed by using the first-principles ultrasoft pseudopotential method based on the density functional theory as implemented in the CASTEP package.[10] The pseudopotentials for Zn, O, S, Se and Te atoms are generated according to the scheme of generalized gradient approximation (GGA) in the Perdew and Wang (1991) form.[11] In our calculations, Zn 4s, 4p, 3d orbitals and X outmost s and p orbitals (i.e. 2s2p for O, 3s3p for S, 4s4p for Se and 5s5p for Te) are included as part of the valence states. The basis sets of the cutoff energy and the k-point meshes are 380 eV and 6×6×6, respectively. The iterative convergence is 5.0×10^{-7} eV/atom.

The lattice parameters of ZnX at ground states are obtained by full geometry optimizations of cell parameters. The procedure of the optimization is an analytical equation of state expression according to the third-order Birch–Murnaghan equation.[12] The calculations of Zn_4X_3M are performed by using the full structural relaxations in 2×2×1 super-cell models.

Fundamentally, all the micro-optical spectra could be derived from the spectra of the real and imaginary parts of the dielectric function. Here, the imaginary part ε_2 is calculated using the momentum matrix elements for occupied (v) and unoccupied (c) electronic states within the selection rules,[13]

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}|\langle\Psi_k^c|\hat{\mu}\cdot\boldsymbol{r}|\Psi_c^v\rangle|^2\delta(E_k^c-E_k^v-\hbar\omega), \quad (1)$$

where e is the elementary charge, $\hat{\mu}$ is the vector defining the polarization of the incident, $\boldsymbol{r}$ is the position operator, Ω is the volume of the unit cell, ε_0 is the dielectric constant, E_k^v and E_k^c are energies of occupied and empty electronic states, respectively. The matrix elements of the position operator[14] are

$$\langle\Psi_k^c|\boldsymbol{r}|\Psi_k^v\rangle = \frac{1}{\mathrm{i}\omega m}\langle\Psi_k^c|\boldsymbol{P}|\Psi_k^v\rangle + \frac{1}{\hbar\omega}\langle\Psi_k^c|[V_{nl},\boldsymbol{r}]|\Psi_k^v)\rangle. \quad (2)$$

Here, $\boldsymbol{P}$ is the momentum operator, $\boldsymbol{r}$ is the position operator, m is the electron mass, V_{nl} is the nonlocal pseudopotential. The real part ε_1 can be evaluated from ε_2 by means of Kramer–Krönig transform. Then, the optical properties, such as the loss function (L), can be obtained using the following equation,

$$L(\omega) = \varepsilon_2/[\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)]. \quad (3)$$

3. Results and discussions

3.1. Electronic structures

The optimized unit cell volumes (in Å^3) are 24.09, 39.59, 45.67, and 56.95 for ZnO, ZnS, ZnSe, and ZnTe, respectively, which are comparable to the values of 23.85, 39.59, 45.51, and 56.85 for those compounds calculated from available theoretical[15] or experimental[16] parameters.

The calculated partial density of states (PDOS) for ZnX is shown in Fig.1(a). Valence states of X s are out of this figure in the range of about $-20-12$ eV. The orbital levels change as the atomic number of X varies. As demonstrated in Fig.1(a), with the increase of atomic number of X, the orbital energy difference $E_{\mathrm{d-p}}$ between Zn d and X p in the valence band region increases, as shown by the data of 0.2986, 1.6236, 1.7865, and 2.0605 eV for ZnO, ZnS, ZnSe and ZnTe, respectively. Meanwhile, the Zn d-X p hybridization decreases. This implies that with increasing atomic number of X, the repulsion between Zn d and X p increases, leading to the reduction of the Zn d-X p interaction. Due to such reduced orbital interactions, charge transfer from the cation to anion ion will be cut down as reported in Ref.[17], where Zn_{Te} is a triple acceptor in ZnTe while Zn_{Se} is a double one in ZnSe. On the contrary, also shown in Fig.1(a), with the increase of atomic number of X, the orbital energy difference between Zn s and X p in the valence band region almost keeps unchanged with only the enhancement of s-p hybridization, and the value of the main peak of Zn s increases from 0.2881 N_e/eV in ZnO to 1.3346 N_e/eV in ZnTe. These electronic orbital interaction changes from natural n-type material ZnO to natural p-type material ZnTe are in accordance with those from ZnX

to group-V (n- type dopants) doped ZnX as well as from group-VII (p-type dopants) doped ZnX to ZnX. Taking ZnS as an example, when doping with group-V element N or Sb, compared with the PDOS of ZnS in Fig.1(a), Zn d-S p energy difference in Zn_4S_3N and Zn_4S_3Sb increases as their hybridization decreases, as shown in Fig.1(b). While Zn d-S p energy difference in group-VII-doped Zn_4S_3Cl and Zn_4S_3I decreases as their hybridizations increases in comparison with the PDOS in ZnS. On the other hand, Zn s and X p hybridization in both group-V (N and Sb)-doped and group-VII (Cl and I)-doped systems decreases. Nevertheless, the hybridization in Cl and I-doped systems reduces more than that in N and Sb-doped systems. These results indicate that both Zn d-X p and Zn s-X p electronic orbital interactions are important in the conductive properties of ZnX, with the dominant effect of Zn d-X p electronic orbital interaction. From this point of view, if we partially substitute Zn with Mg in ZnO, the p-type doping tendency will increase due to the reduction of Zn d states. This might be the reason why some ZnMgO alloys can be doped as p-type ones.[18]

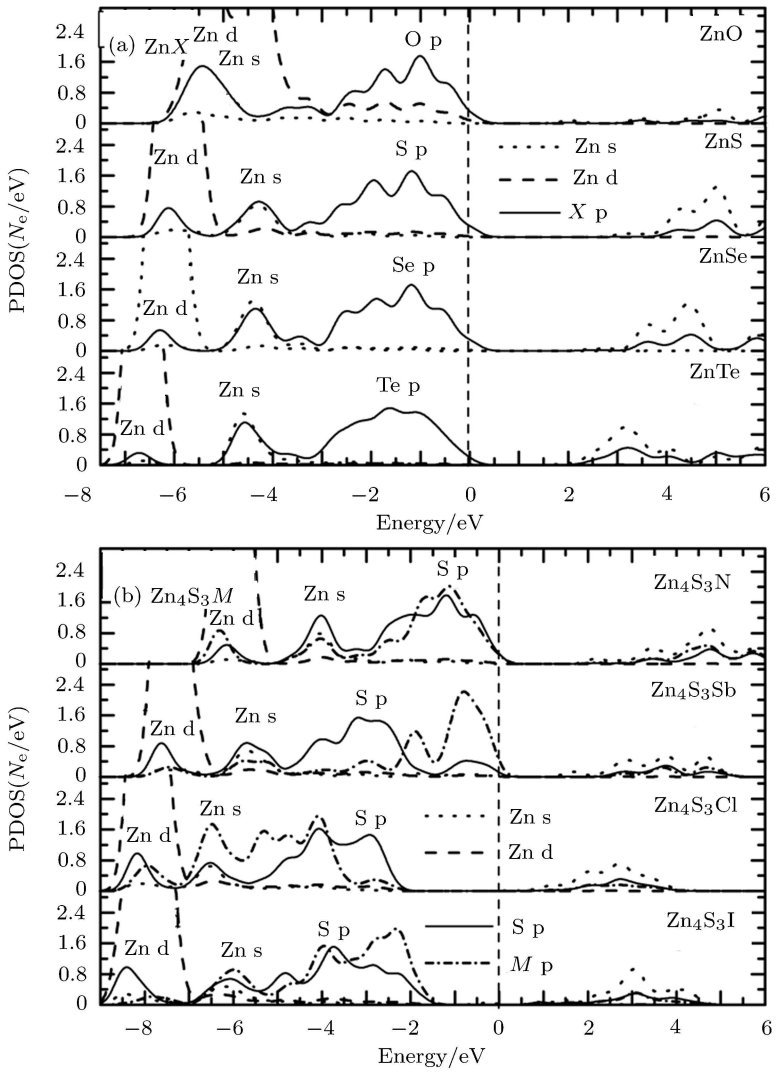


Fig.1. Partial density of states for ZnX (X=O, S, Se or Te) and Zn_4S_3M(M=N, Sb, Cl or I). The vertical dashed lines represent the Fermi levels.

3.2. Optical properties

The optical spectra of ZnX show that with the increase of atomic number of X, the main peaks of both the real (ε_1) and imaginary (ε_2) parts shift to lower energy region. As demonstrated in Figs.2(a) and 2(b), the main peaks of both ε_1 and ε_2 of ZnS lie respectively at about 3.8239 and 6.1071 eV, higher than those of ZnTe's, which are 2.5009 and 4.6228 eV. This is similar to the results obtained by Ouyang *et al* in

Ref.[19], where they showed similar shift of the dielectric function for $Zn_{1-x}Co_xX$ system. Since the optical behaviours occur with electronic trapping between occupied (valence) and unoccupied (conduction) states within $\hbar\omega = E_k^c - E_k^v$ and electronic dipole matching (refer to the PDOS of ZnS and ZnTe in Fig.1(a)), the corresponding electronic trappings in ZnS and ZnTe are Zn s→S p and Zn s→Te p.

In Fig.2, ε_1 and ε_2 spectra of $Zn_4S_{4-y}M_y$ and $Zn_4Te_{4-y}M_y$ (M=N, Sb, Cl or I; $y = 0$ or 1) are also shown. Compared with the spectra of ZnS and ZnTe, there are more peaks in $Zn_4S_{4-y}M_y$ and $Zn_4Te_{4-y}M_y$, and almost all the spectral peaks shift to lower energy region, with only few exceptions, due to the effect of the dopant states on the electronic trappings. As shown in Fig.2, there appears only one peak in the spectrum of ZnS or ZnTe, but there are at least two peaks in that of Zn_4S_3M or Zn_4Te_3M. The main peak of the doped systems shifts to lower energy region compared with that of ZnS or ZnTe, with the only exception of Zn_4S_3N. This identifies the different influences of different dopants on the bulk electronic structures. As shown in Fig.1, electronic trapping energy from S p state in the valence band to Zn s state in the conduction band is about 6.1884 eV in ZnS, which is larger than 5.9150 eV in Zn_4S_3N and smaller than the values of 6.9491, 6.7545, and 6.7892 eV in Zn_4S_3Sb, Zn_4S_3Cl, and Zn_4S_3I, respectively.

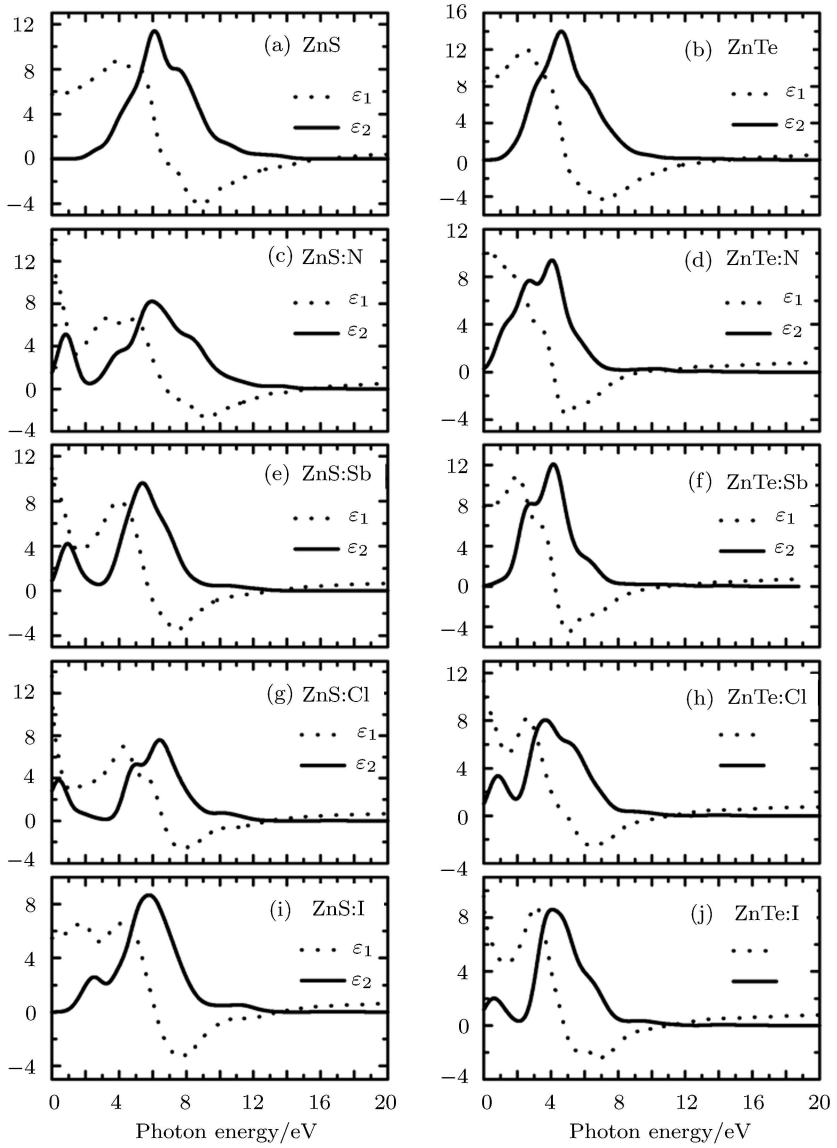


Fig.2. Real and imaginary parts of spectra of the real and imaginary parts of the dielectric function for $Zn_4S_{4-y}M_y$ and $Zn_4Te_{4-y}M_y$ (M=N, Sb, Cl or I; y=0 or 1). Here ε_1 and ε_2 represent the real and imaginary parts of the dielectric function.

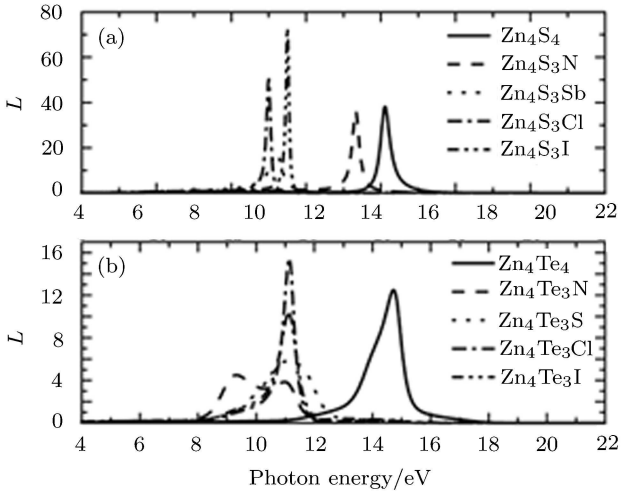


Fig.3. Spectra of energy loss functions for $Zn_4S_{4-y}M_y$ and $Zn_4Te_{4-y}M_y$ (M=N, Sb, Cl or I; $y = 0$ or 1).

The carrier types also determine the features of the optical spectra for the doped and undoped systems, which could be clearly seen in L spectra. The spectrum shapes of Zn_4S_3N and Zn_4S_3Sb in Fig.3 are similar to that of ZnS, while those of Zn_4Te_3N and Zn_4Te_3Sb are quite different from that of ZnTe. On the contrary, the spectrum features of Zn_4S_3Cl and Zn_4S_3I are much different from that of ZnS compared with the L differences between Zn_4Te_3Cl (Zn_4Te_3I) and ZnTe. Moreover, with the increase of dopant atomic number, the directions of spectrum shift of group-V-doped and group-VII-doped systems are different. As shown in Fig.3, the peak of Zn_4S_3N lies right to that of Zn_4S_3Sb, while the peak of Zn_4S_3Cl is located on the left side of Zn_4S_3I's.

4. summary

In summary, we have studied the electronic orbital interactions in $Zn_4X_{4-y}M_y$(X=O, S, Se, or Te; M=N, Sb, Cl, or I; $y = 0$ or 1) by means of first-principles calculations using a pseudopotential plane-wave method. The results show that Zn d-X p orbital interaction plays an important role in the p-type conduction possibility. Reducing Zn d-X p orbital interaction leads to the increase of the p-type conduction tendency. Analysis of the optical spectra indicates that with the increase of atomic number of X, the main peaks of the optical spectra shift to lower energy region. Furthermore, different carrier-doped compounds exhibit different characteristics. The spectra of p- (n-) type-doped systems are similar to that of the corresponding undoped natural n- (p-) type materials, but different from the spectra of the corresponding undoped natural p- (n-) type pure ones.

References

[1] Üzgür Ü, Alivov I, Liu C, Teke A, Reshchikov M A, Doğan, Avrutin V, Cho S J and Morkoc 2005 *J. Appl. Phys* **98** 041301
[2] Neumark G F 1989 *Phys. Rev. Lett.* **62** 1800
[3] Look D C, Farlow G C, Reunchan P, Limpijumnong S, Zhang S B and Nordlund K 2005 *Phys. Rev. Lett.* **95** 225502
[4] Park C H, Zhang S B and Wei S H 2002 *Phys. Rev.* B **66** 073202
[5] Chadi D J 1994 *Phys. Rev. Lett.* **72** 534
[6] Li J, Wei S H, Le S S and Xia J B 2006 *Phys. Rev.* B **74** 081201
[7] Lee G D, Lee M H and Ihm J 1995 *Phys. Rev.* B **52** 1459
[8] Wei S H and Zunger A 1998 *Appl. Phys. Lett.* **72** 2011
[9] Kato H, Sano M and Miyamoto K 2002 *J. Crys. Growth* **237** 538
[10] Segall M D, Lindan P J D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys. : Cond. Matt.* **14** 2717
[11] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244
[12] Birch F 1978 *J. Geophys. Res.* **83** 1257
[13] Ehrenreich H 1959 *Phys. Rev.* **115** 786
[14] Read A J and Needs R J 1991 *Phys. Rev.* B **44** 13071
[15] Zaoui A and Sekkal W 2002 *Phys. Rev.* B **66** 174106
[16] *Physics of II-V and I-VII compounds, Semimagnetic Semiconductors* edited by K. H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. b (Springer, New York, 1982)
[17] Jansen R W and Sankey O F 1989 *Phys. Rev.* B **39** 3192
[18] Heo Y W, Kwon Y W, Li Y, Pearton S J and Norton D P 2004 *Appl. Phys. Lett.* **84** 3474
[19] Ouyang C Y, Xiong Z H, Ouyang Q Z, Liu G D, Ye Z Q and Li M S 2006 *Chin. Phys.* **15** 1009