First-principles calculation of the electronic band of ZnO doped with C*

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Abstract: Using the first-principles approach based upon the density functional theory (DFT), we have studied the electronic structure of wurtzite ZnO systems doped with C at different sites. When Zn is substituted by C, the system turns from a direct band gap semiconductor into an indirect band gap semiconductor, and donor levels are formed. When O is substituted by C, acceptor levels are formed near the top of the valence band, and thus a p-type transformation of the system is achieved. When the two kinds of substitution coexist, the acceptor levels are compensated for all cases, which is unfavorable for the p-type transformation of the system.

Key words: wurtzite ZnO; first-principles; electronic structure; p-type transformation
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1. Introduction

ZnO is a promising candidate for applications in ultra-violet (UV) optoelectronic devices because of its wide band gap (~3.37 eV) and large exciton binding energy (~60 meV) at room temperature. It can be used in the fields of blue and ultraviolet lasers, light-emitting diodes, and solar cells[1, 2]. The as-grown ZnO is an n-type semiconductor with many donor defects, such as O vacancy (V_O) and interstitial Zn (Zn_i), so it is very difficult to dope ZnO to act as a p-type semiconductor because of the self-compensation by the donor defects. Thus, the development and application of ZnO-based optoelectronic devices are greatly limited due to the lack of ZnO p-n junctions. Therefore, p-type doping of ZnO has become a focus task. ZnO has been doped with group Ⅰ, Ⅴ, and Ⅲ–Ⅴ elements and some valuable results have been obtained. For the doping of ZnO with the group Ⅳ element carbon, many studies on the magnetic properties[3, 4] have been done, but very little attention has been paid to the p-type transformation issue. In 2007, Tan *et al.*[5] studied the effect of C_{Zn} + O_i defect in ZnO, and p-type ZnO films were obtained.

In this paper, we study three kinds of defects in ZnO, namely the substitution of Zn by C, O by C, and the two kinds of substitutes coexisting. Electronic structures of the systems are calculated. The obtained results show that when Zn is substituted by C, the system turns from a direct band gap semiconductor into an indirect band gap semiconductor, and donor levels are formed. When O is substituted by C, acceptor levels are formed near the top of the valence band, and, thus, a p-type transformation of the system is achieved. It is shown that a high acceptor concentration is unfavorable for the p-type transition. When the two kinds of substitutes coexist, the acceptor levels are compensated for all cases, which is unfavorable for the p-type transformation of the system.

2. Model and calculation method

The ideal ZnO has a hexagonal wurtzite structure with the space group P63/mc and C6v-4 symmetry. The cell parameters are $a = b = 0.3249$ nm, $c = 0.5206$ nm, $\alpha = \beta = 90°$, and $\gamma = 120°$. To illustrate the atom coordinates, a $2 \times 2 \times 2$ supercell of the wurtzite ZnO is shown in Fig. 1. It can be seen that the ligand of ZnO is a triangular cone, the side edge length is shorter than the underside edge length, and the length of the bond between the center atom and the cone-top atom is slightly longer than that of the bond between the center atom and the underside atom. The O^{2-} coordination polyhedron is an O-Zn_4 tetrahedron, so it is a Zn^{2+} coordination polyhedron. In the calculation a $2 \times 2 \times 1$ supercell is used because of the capability of our computers.

The calculations are carried out by using the CASTEP package provided by the Material Studios 4.1 by Accelrys. The package is an *ab initio* quantum mechanics codes based on density functional theory. In the package, the ionic potential is substituted by a pseudo-potential, the electronic wave function is expanded by a plane wave, and the exchange and correlative
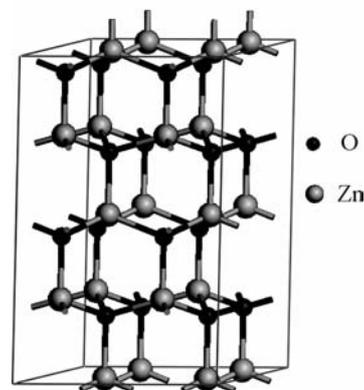

Fig. 1. Supercell of ZnO.

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Table 1. Comparison of the optimized results of the primitive cell of ZnO and the experimental data.

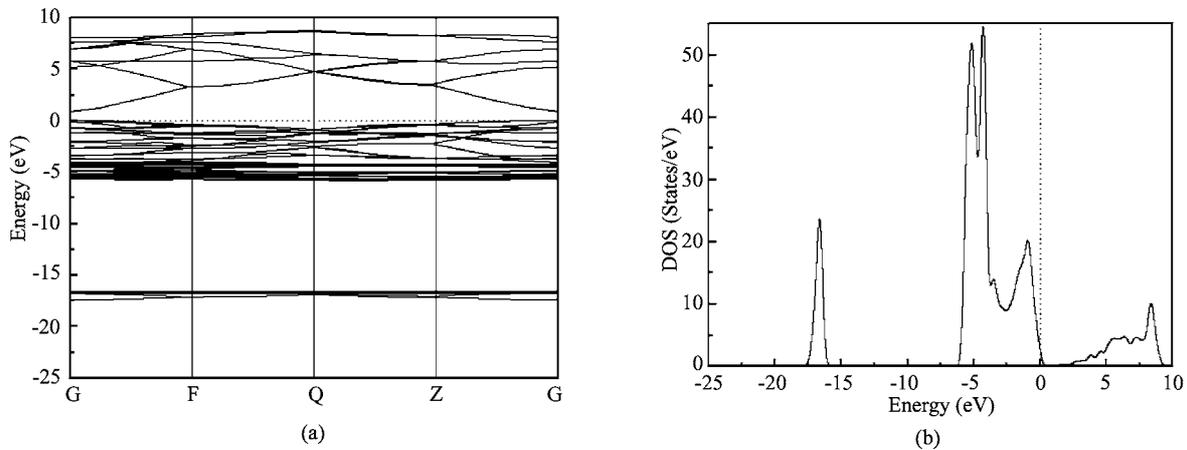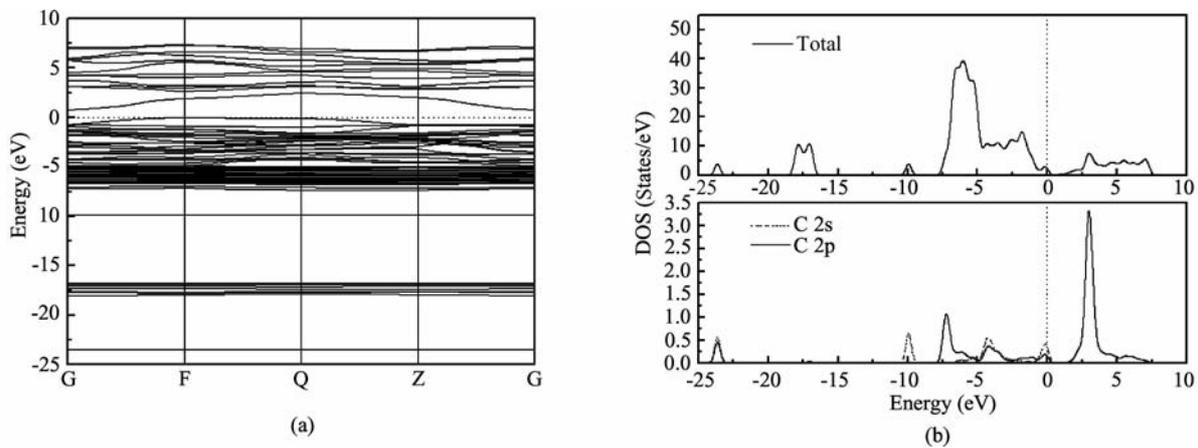|	a (nm)	c (nm)	c/a	V_0 (nm^3)
Calculation value	0.3295	0.5317	1.614	0.049907
Experimental data[6]	0.3249	0.5206	1.602	0.048335

Fig. 2. (a) Band and (b) DOS of ZnO.

Fig. 3. (a) Band and (b) DOS of ZnO with C$_{Zn}$.

potential of electronic-electronic interactions are improved by the generalized gradient approximation (GGA). In our calculation, a $4 \times 4 \times 4$ k–point mesh in the Brillouin zone is used, the cutoff energy of the plane wave is 300 eV, and the calculation precision is set to be 2.0×10^{-5} eV/atom.

3. Results and discussion

First, the supercell is optimized in the calculation. The optimized results of the primitive cell of pure ZnO are shown in Table 1. It is obvious that the optimized geometry parameters are in good agreement with experimental results[6], meaning that our calculation is reasonable.

For comparison, we first calculate the electronic structure of the pure ZnO crystal. The calculated band and density of states (DOS) are shown in Fig. 2. It is evident that the bottom of the conduction band and the top of the valence band are in the same k-point (G); i.e., ZnO is a typical direct band gap semiconductor. The valence band can generally be divided into two regions: the lower valence band within –6.6 to –2.6 eV and the upper valence band within –2.6 to 0 eV. The upper valence

band is mainly contributed by the 2p states of O (O2p), and the lower valence band is chiefly contributed by the 3d states of Zn (Zn3d). The conduction band is primarily contributed by the Zn4s states and the O2p states. Here, the band gap is 0.93 eV, which is in agreement with the theoretical results of other researchers[7], but much smaller than the experimental results (3.37 eV). This difference originates from the GGA approximation adopted in the calculation process; the aberration can be corrected by the scissors approximation.

3.1. Band structure and DOS of ZnO with C$_{Zn}$

We consider the case that one Zn atom is substituted by one C atom in the supercell; i.e., the doping concentration is 12.5%. The band and DOS of the doped system are shown in Fig. 3. Two narrow bands, one nearby –23.6 eV and the other nearby –10 eV, are introduced by the C$_{Zn}$. The former is contributed by C2s states and C2p states, and the latter is contributed by C2s states. The two narrow bands are far away from the valence band, and they interact with the valence band weakly. Compared with pure ZnO, the conduction band minimum is still at the G-point, while the valence band maximum

(a)

(b)
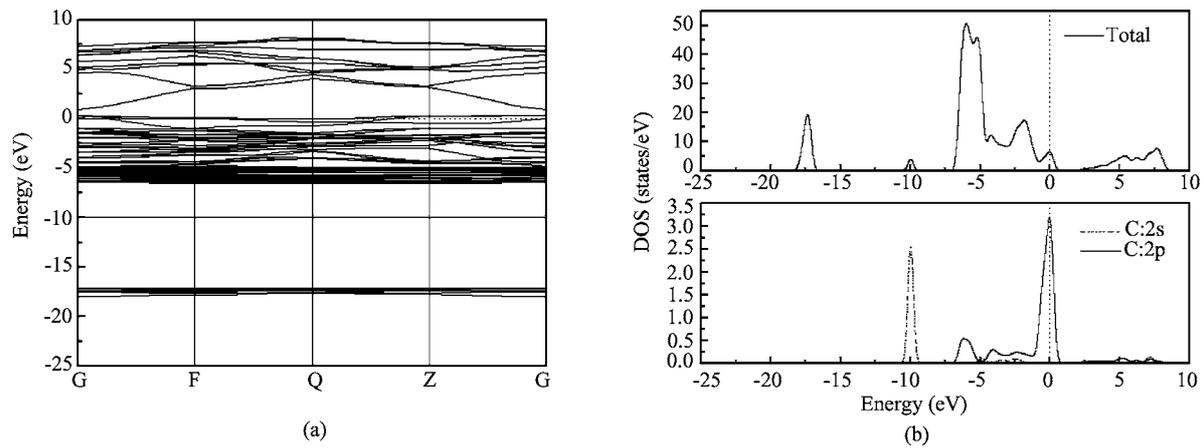
Fig. 4. (a) Band and (b) DOS of ZnO with C_O.

(a)

(b)
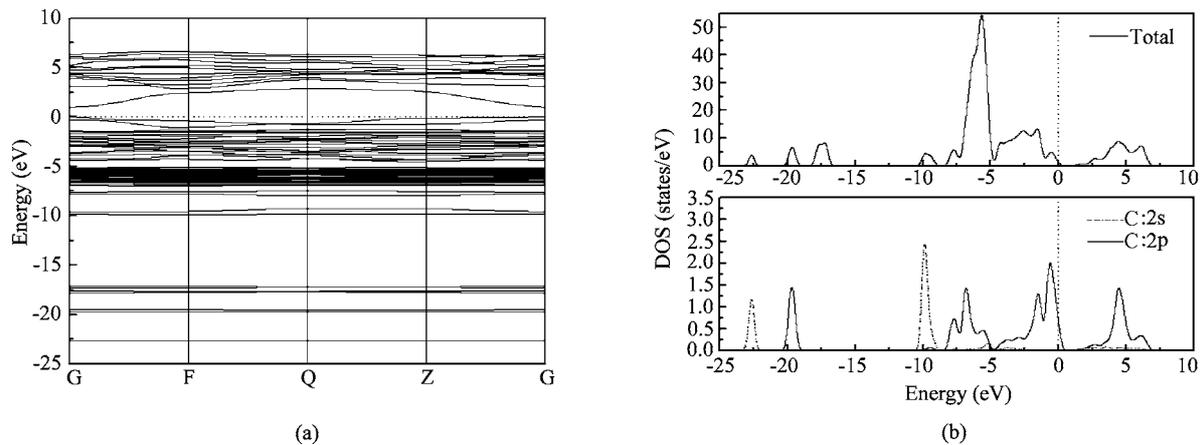
Fig. 5. (a) Band and (b) DOS of ZnO with C_O–C_{Zn}.

is shifted from the G-point to the F-point; i.e., the system turns into an indirect band gap semiconductor. Meanwhile, the band gap reduces slightly. Donor levels are close to the bottom of the conduction band, so C_{Zn} is an n-type doping.

3.2. Band structure and DOS of ZnO with C_O

We consider the case that one O atom is substituted by one C atom in the supercell; i.e., the doping concentration is 12.5%. The band and DOS of the doped system are shown in Fig. 4. A new narrow band exists nearby –10 eV, which is contributed by C2s states. In addition, the DOS near the Fermi level increases because of the contribution by C2p states. More importantly, at about 0.33 eV above the top of the valence band, acceptor levels appear. Thus, a p-type transformation can be realized by C_O. It should be pointed out that the acceptor levels formed by C_O are shallower than those found for Ag_{Zn}[8, 9] and N_O[10, 11], but are still deep levels. Just like in the cases of Ag_{Zn} and N_O, it is difficult to achieve a high quality p-type transformation only by C_O. Furthermore, we have also considered cases with acceptor concentrations of 25% and 37.5%, and the obtained results show that a high acceptor concentration is unfavorable for the p-type transition.

3.3. Band structure and DOS of ZnO with a coexistence of C_O and C_{Zn}

We consider the case that one Zn atom and one O atom

are simultaneously substituted by C atoms in the supercell, and the substituted Zn atom and O atom are adjacent in the plane perpendicular to the c axis. The band and DOS of the doped system are shown in Fig. 5. The main contribution by C_O lies near the top of the valence band; the contribution by C_{Zn} to the conduction band decreases, while the contribution to the valence band increases significantly, and the valence band is broadened. Compared with the case of C_{Zn}, the top of the valence band in the coexistence case transfers from the F-point to the G-point, so the system turns back into a direct band gap semiconductor. It is worth noting that the acceptor levels contributed by C_O disappear because of the compensation effect of C_{Zn}. Furthermore, we have also considered the situations that the substituted Zn and O atoms are second nearest neighbors in the plane perpendicular to the c axis, and situations where they are adjacent and second nearest neighbors along the direction parallel to the c axis. The obtained results show that the acceptor levels are totally compensated for all the cases.

3.4. Charge density and population

The charge density distribution of pure ZnO and ZnO with C_O (concentration 12.5%) system is shown in Fig. 6, and the corresponding population number and bond lengths are listed in Table 2. For the pure ZnO, the bond between Zn and O (Zn–O) is a covalent bond with a weak ionic bond com-
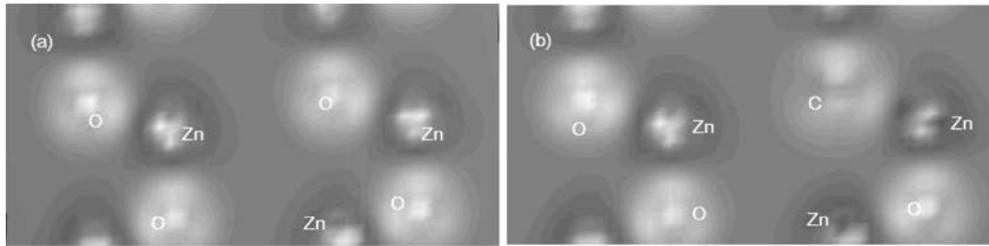
Fig. 6. Charge density distribution of (a) ZnO and (b) ZnO with C_O.

Table 2. Population number (N) and bond length (L).

Bond	ZnO		ZnO with C_O			
	Zn–O^1	Zn–O^2	Zn–C^1	Zn–C^2	Zn–O^1	Zn–O^2
N	0.39	0.38	0.74	0.69	0.36	0.39
L (nm)	0.2025	0.2001	0.1996	0.1990	0.2031	0.2034

(1) Parallel to c axis; (2) Perpendicular to c axis

ponent. A charge density distribution change takes place when O is substituted by C. The ionic part of the Zn–C bond parallel to the c axis (Zn–C^1) is weaker than that of the Zn–C bond perpendicular to the c axis (Zn–C^2). The covalency of the Zn–C bond is stronger than that of the Zn–O bond in the undoped case, and the bond length decreases. The bond length of the Zn–O bond increases compared with the undoped case. The population of the Zn–O^2 bond changes little, while the population of the Zn–O^1 decreases and the bond covalency becomes weaker. The interactions between a C atom and the surrounding atoms is reduced, and both the Zn–C bond and the adjacent Zn–O bond tend to break. Thus, the electrons are released, and holes are formed around the impurities. As a result, the acceptor levels are formed because of the exclusive effects among holes. Similar cases may occur for the p-type doping of other wide band gap semiconductors.

4. Conclusion

Using a first-principles method, we have studied the electronic structure of doped wurtzite ZnO systems with C at different sites. The obtained results show that when Zn is substituted by C, the system turns from a direct band gap semiconductor into an indirect band gap semiconductor, and donor levels are formed. When O is substituted by C (at an acceptor concentration of 12.5%), acceptor levels are formed about 0.33 eV above the top of the valence band; thus, a p-type transformation of the system is achieved. However, a higher acceptor concentration is unfavorable for the p-type transition. When the two kinds of substitution coexist, the acceptor levels are compensated for all cases, which is unfavorable for the p-type transformation of the system.

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