First-principles calculations of electronic structure and optical properties of boron–phosphorus co-doped zinc oxide

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ABSTRACT

This paper presents the electronic structure and optical properties of boron–phosphorus co-doped zinc oxide ((B, P) codoped ZnO) systems employing first principles calculations based on density functional theory. In the (B, P) codoped ZnO systems, dopants prefer to be located on the nearest-neighbor sites in the same (00l) plane forming B_{Zn}–P_O complex with binding energy of -1.92 eV; some hole sates appear above the valence band maximum. With increase in P concentration, P 3p states become more and more delocalized. The calculated optical properties indicate that strong optical transitions in lower energy region occur; the intensities and positions of these peaks are P concentration-dependent, which could be ascribed to the electronic transitions between P 3p and Zn 4s states. Moreover, the absorption coefficients and other optical constants of the (B, P) codoped ZnO systems, such as reflectivity, refractive index, and loss function, are also discussed.

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1. Introduction

ZnO has considerable potential for applications in optoelectronic devices due to its wide direct band gap, and high exciton binding energy. In addition, it is possible to tune the band gap by doping [1,2]. As grown, ZnO acts as an n-type semiconductor, and it is difficult to produce p-type ZnO that is essential for realizing ZnO based optoelectronic devices. In general, doping destroys the local symmetry, and the chemical mismatch between the host and dopant may result in deep defect levels in the band gap. To reduce these effects, significant efforts have been made. Yan et al. [3] proposed an approach of codoping which uses one donor and one acceptor to form a passive complex, which creates fully occupied impurity bands above the valence band maximum (VBM). With further doping, acceptors will bind to the complex and effectively dope the fully occupied impurity bands. Furthermore, the formation of the acceptor–donor pairs also stabilizes the defects. Researches have been

reported about the codoping approach in ZnO, which mainly focus on N acceptor [4,5]. P is also considered to be one of the suitable dopants. Although p-type conduction can be realized with P-doping in ZnO by several methods, the reliability of the p-type behavior remains questionable [6–10]; the electronic structure and optical properties have not been completely understood. Therefore, theoretical investigations of the P and donors codoped ZnO systems are necessary. First-principle calculations of optical properties of the codoped ZnO systems are particularly helpful for understanding their optical transition mechanism.

In this paper, we report our theoretical investigation of the B and P codoped ZnO systems using first principles calculations based on density function theory (DFT). A lot of researches have been reported that B atom in ZnO prefer to substitute Zn atom [11–14]. With further introduction of P atoms, we find that the substitutional incorporation of B on the Zn site acts as donors that have a tendency to form passive complexes with P atoms located on the nearest-neighbor oxygen sites. To investigate the codoping effect of B and P in ZnO, five different configurations are considered. The electronic structures and optical properties of the codoped ZnO systems are calculated; the results are

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compared with corresponding experimental and other theoretical results.

2. Calculation models and methods

All calculations were performed with CASTEP code of plane-wave ultrasoft pseudopotentials [15]. The generalized gradient approximation with the Perdew–Burke–Ernzerh scheme [16] is adopted for the exchange–correlation potential. O $2s^22p^4$, Zn $3d^{10}4s^2$, B $2s^22p^1$, and P $3s^23p^3$ as the valence-electron configurations were used to describe the electron–ion interaction. The electron wave function is expanded in plane waves with a cutoff energy of 370 eV, and a Monkhorst-Pack grid [17] with parameters of $4 \times 4 \times 2$ is used for irreducible Brillouin zone sampling. Actually, the extensive tests were also performed. With increase in cutoff energy, the lattice constants and total energies have no obvious change, which is similar to the results of Yan et al. [18]. Then we fixed the cutoff energy at 370 eV and increased the k point mesh from $4 \times 4 \times 2$ to $4 \times 4 \times 4$, $5 \times 5 \times 3$ and $7 \times 7 \times 4$, we found that the differences in the total energies are accurate to within 0.01 eV, and there is little change both in the imaginary part of dielectric functions $\varepsilon_2(\omega)$ and the absorption spectrum. Actually, Lee et al. [7] had tested a larger number of k points, and found that the difference in the total energies is accurate to within 0.02 eV between $3 \times 3 \times 3$ and $2 \times 2 \times 2$ meshes. Many other investigations show that the $4 \times 4 \times 2$ k-point mesh is sufficient for our calculations [7,19–21]. The ZnO supercells contain 32 atoms, and the same number has been used in other reports [18,22–25]. The total energy is converged to lower than 2×10^{-5} eV/atom, and the force on each atom converges to less than 0.05 eV/Å. Then electronic structures and optical properties are calculated on the basis of the lattice structures optimized.

To determine whether it is energetically preferred that two dopants bind, e.g., B_{Zn} and P_O in the neutral charge state, we calculated the binding energy which is defined as

$$E_b = E_{tot}(B_{Zn}-P_O) + E_{tot}(ZnO) - E_{tot}(B_{Zn}) - E_{tot}(P_O) \quad (1)$$

where E_{tot} ($B_{Zn}-P_O$), E_{tot} (B_{Zn}) and E_{tot} (P_O) are the total energies for supercells containing defects $B_{Zn}-P_O$, B_{Zn}, and P_O, respectively. A negative value of E_b corresponds to a metastable or stable bound dopant pair when both are present in the system. The extension of Eq. (1) to other complexes is straightforward.

3. Results and discussion

3.1. Structural properties of B and P codoped ZnO systems

The optimized lattice constants are $a = 3.282$ Å, $c = 5.315$ Å for pure ZnO, as shown in Table 1, which are in good agreement with the JCPDS file of ZnO ($a = 3.253$ Å, $c = 5.213$ Å). Compared to the experimental band gap of 3.37 eV, the calculated band gap of 0.73 eV is underestimated, which is attributed to the well-known intrinsic factor of DFT. But the value is consistent with other DFT-LDA or DFT-GGA studies, which give values in the range of 0.7–0.9 eV [26–29]. For single B dopant in ZnO, the radius of B

Table 1

Calculated lattice constants a, c and the binding energies E_b for the defect complexes in different ZnO configurations. The binding energies of the defects are computed with respect to the defect combinations in the parentheses.

Configuration	a (Å)	c (Å)	E_b (eV)
ZnO	3.282	5.315	–
(B_{Zn}–P_O)	3.286	5.293	−1.92 (B_{Zn}+P_O)
(B_{Zn}–2P_O)	3.315	5.498	−1.14 [(B_{Zn}–P_O)+P_O]
(B_{Zn}–3P_O)	3.338	5.497	−1.29 [(B_{Zn}–2P_O)+P_O]
(B_{Zn}–4P_O)	3.362	5.632	−0.75 [(B_{Zn}–3P_O)+P_O]

ion is so small (B^{3+}, about 0.23 Å) [30–32], and two possibilities are considered: (1) the substitution of B into Zn site (B_{Zn}), and (2) B exists in the interstitial site (B_i). According to references [4,5], the formation energies of the defects are calculated. The estimations show that the formation energy of B_i is higher than that of B_{Zn} by about 2.04 eV, which indicates that B at Zn site is energetically favorable. Actually, the theoretical and experimental results show that B atom prefers to substitute Zn atom in ZnO [11–14]. Therefore, we mainly consider substitutional B on the Zn site (B_{Zn}) in this paper. Because the radius of B^{3+} (about 0.23 Å) is smaller than that of Zn^{2+} (about 0.74 Å) [30–32], the average lattice constants change by −0.02 Å for a and −0.10 Å for c after structural optimization. These structural parameters are consistent with other calculated results [12]. With incorporation of P atom, many researches show that P atom prefers to substitute Zn or O atom in ZnO systems [33–37]. Therefore, the configuration of P occupying Zn site is tested based on the B doped ZnO supercell. Two different positions of P atom are considered, the "near" configuration, in which P and B atoms in the same unit cell are separated by a single O, and the "far" configuration, in which they are connected via – O–Zn–O-bond. However, the results show that these configurations undertake serious lattice distortion and unacceptable mismatch around P atom. The estimated binding energies are about −0.82 and −0.78 eV for the "near" and "far" models, relative to the single defects B_{Zn} and P_{Zn}, respectively, which indicate that the substitution of P on Zn site is unfeasible in these configurations. Considering the radii of B^{3+} (about 0.23 Å), P^{3+} (about 0.44–0.58 Å) and P^{5+} (about 0.31–0.34 Å), which are smaller than that of Zn^{2+} (about 0.74 Å), while the radius of P^{3-} (about 1.80–2.12 Å) is larger than that of O^{2-} (about 1.38–1.40 Å) [30–32,35]. Thus, the formation of defects (B_{Zn}–P_O) could expect some structure relaxation in (B, P) codoped ZnO systems. Following the approach proposed by Yan et al. [3], the interaction between B_{Zn} and P_O is investigated and it is found that dopants prefer to be located on nearest-neighbor sites in the same (00l) plane, as shown in Fig. 1(a). This configuration is referred to as B_{Zn}–P_O, corresponding to doping levels of 6.25 at% for both B and P. The binding energy is −1.92 eV, relative to the single defects B_{Zn} and P_O. The energy of the structure with B_{Zn} and P_O on the nearest-neighbor sites along the c-axis is about 0.86 eV higher, and the energy of the configuration with B_{Zn} and P_O "far apart" (connected via – O–Zn-bond) is 1.00 eV higher. We therefore focus on the more stable configuration of the B_{Zn}–P_O for further calculations. With increase in P concentration, the other configurations shown in Fig. 1(b), (c)