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Electronic structure and optical properties of substitutional and interstitial phosphor-doped ZnO

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ABSTRACT

Using first-principles method, electronic structure and optical properties of phosphorus-doped ZnO for the possible substitutional (P_{Zn}, P_O) and interstitial (P_{tet}, P_{oct}) doping are investigated. P_O gives p-type conductivity, but others show n-type. P_O and P_{tet} has a significant difference in optical properties due to the contribution of P 3p states at Fermi level.

1. Introduction

As a wide band gap semiconductor, ZnO has recently attracted great attention because of potential applications in optical and optoelectronic devices, such as lasers [1], light emitting diodes [2–4], transparent electrodes in solar cells [5] and photodetectors [6]. Experimentally, n-type ZnO thin film with good conductive properties can be easily obtained by doping impurities in pure ZnO [7–11]. However, it is difficult to fabricate p-type ZnO due to a large number of native defects such as Zn interstitials (Zn_i) and/or O vacancies (V_O) [12]. At present, attractive acceptor-state candidates for ZnO are group-V elements substituted at the O site. Several groups have attempted to achieve p-type ZnO with group-V elements using different experimental methods [13–17]. Some researchers found that N-doped ZnO could be unstable and difficult to be repeated [18–20]. More recently, P monodoped [21,22], (P–In) [23] and (P–N) [24] codoped ZnO have realized p-type conductivity. P-doped ZnO having the trends for both n- and p-type have been observed in experiments [25–27]. The lack of stable p-type materials is still the key issue which hinders the development of ZnO-based optoelectronic devices [28,29]. To reveal the origins of the characters, first-principles calculations were performed to study the electronic structures of native and P-related defects and in pure and P-doped ZnO [28–33]. Based on first-principles calculations, the theory for large-sized-mismatched group-V dopants [28] and a P_{Zn}–$2V_{Zn}$ complex contributing to p-type doping efficiency in P-doped ZnO [29] have been presented. More recently, Tian et al. found that P_{Zn}–$4N_O$ complexes may have lower formation energy than that of P_{Zn} under Zn-rich condition, which helps improving the p-type conductivity in ZnO [33]. We have performed first-principles calculations to reveal the contribution of P_{Zn} and P_O to the conductivity type of P-doped ZnO [34]. In fact, the possible positions (interstitial and substitutional) of P in ZnO should be taken into account [35]. It is a pity that there is not more information about interstitial P-related defects in the previous first-principles calculations. Moreover, some groups have experimentally investigated the optical properties of P-doped ZnO [25,36,37], yet little microscopic information on the formation mechanism has emerged [15].

In the present Letter, we report on a density functional study of the electronic and optical properties of P-doped ZnO for the substitutional (P_{Zn}, P_O) and interstitial (P_{tet}, P_{oct}) doping configurations. We firstly examined the formation energies of the different doping sites, and it has been found that P_O is more difficult to achieve and P_{Zn} is energetically favorable. Secondly, according to band structures and densities of state of pure and P-doped ZnO, we found that a substitutional P at an O site forms a deep acceptor level and a substitutional P at a Zn site behaves as a donor. P atoms at both tetrahedral and octahedral interstitial sites contribute to n-type conductivity. Thirdly, the optical properties are determined by the band structures, and the optical constants, including the optical absorption, reflectivity, refractive index, extinction coeffi-

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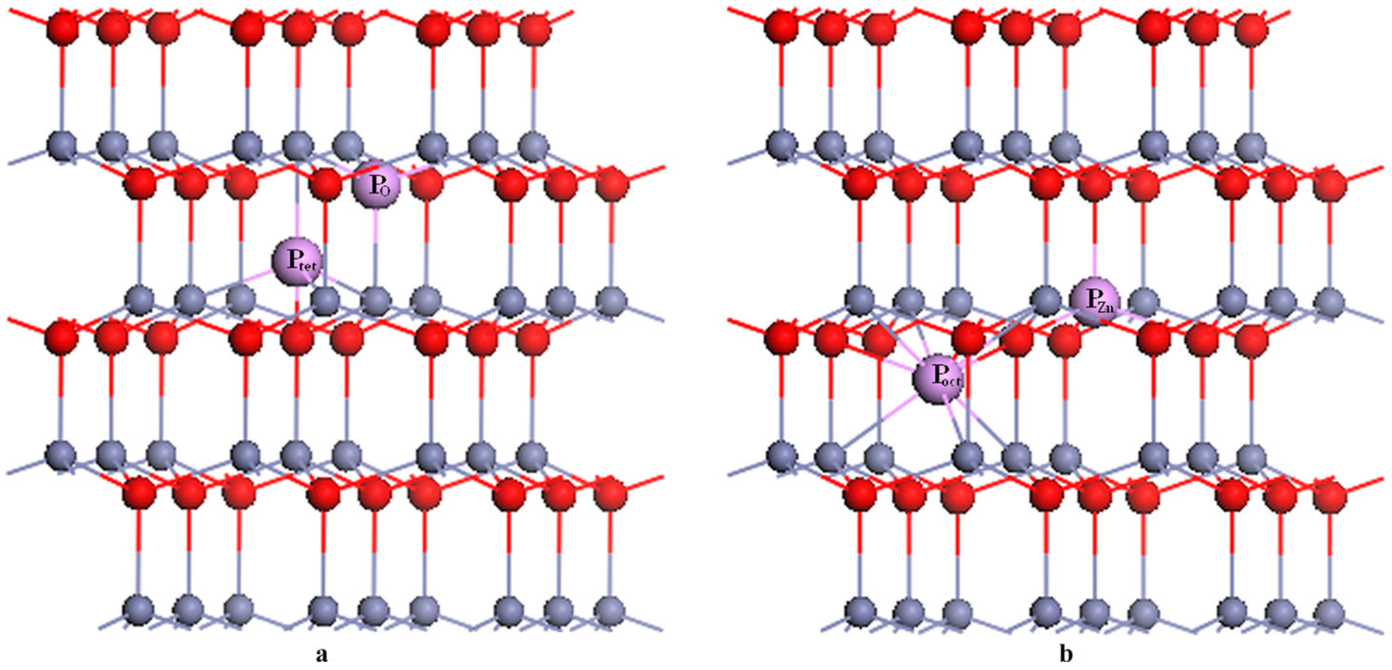

Fig. 1. The supercell atomic structure of P-doped ZnO used in the calculations. Gray balls indicate Zn and red balls represent O. Here, P_O and the interstitial site as the center of tetrahedral (P_{tet}), and P_{Zn} and the octahedral interstitial site (P_{oct}) are indicated in (a) and (b), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

cient and energy loss function, have been discussed for pure and P-doped ZnO. Compared with the other doping configurations, P at O site and tetrahedral interstitial site will result in a remarkable difference in optical properties, such as the optical absorption intensity in visible-UV range.

2. Computational details

The calculations are performed with CASTEP (Cambridge serial total energy package) code [38], which is based on the density functional theory using a plane-wave pseudopotential method. This method can be used to calculate the periodic structural materials. In this Letter, we used the Perdew–Burke–Ernzerhof (PBE) [39] to describe the exchange-correlation function in the scheme of generalized gradient approximation (GGA) and selected the ultrasoft pseudopotential (USP). O $2s^2 2p^4$, Zn $3d^{10} 4s^2$ and P $3s^2 3p^3$ as the valence-electron configurations were used to describe the electron–ion interaction. We employed a supercell containing 36 host atoms in the wurtzite structure. The four dopant sites of P atoms including substitutional and interstitial sites are indicated as Fig. 1. In the optimization process, a plane wave basis set with an energy cutoff of 340 eV was used to expand the electronic wave functions. Supercell structures were fully relaxed and the free movement of the atoms in any direction was allowed and no symmetry constraint was imposed. In the procedure of calculation, the atomic coordinates were optimized to achieve the energy minimization. A $4 \times 4 \times 2$ Brillouin-zone k-point sampling was used in the calculations. The convergence in energy, maximum force, maximum stress, and maximum displacement tolerances were set as 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively.

The formation energies of the P dopants at substitutional and interstitial dopant sites in ZnO are expressed respectively, by

$$E^f(P_s) = E_{def}(P_s) - E_{per}(ZnO) - (\mu_P - \mu_s) \tag{1}$$

$$E^f(P_i) = E_{def}(P_i) - E_{per}(ZnO) - \mu_P \tag{2}$$

where $E^f(P_s)$ and $E^f(P_i)$ indicate the formation energies of substitutional and interstitial P defects, respectively. $E_{def}(P_s)$ and $E_{def}(P_i)$ are the total energies of a ZnO supercell containing substitutional and interstitial P defects, respectively. $E_{per}(ZnO)$ is the total energy of a perfect supercell of ZnO. μ_P is the phosphor chemical potential, and μ_s ($s = Zn$ and O) denotes the corresponding atomic chemical potential. For ZnO, the chemical potential $\mu_O = \frac{1}{2}E(O_2)$ and $\mu_{Zn} = E(Zn)$ is given by the total energy per each Zn atom in bulk zinc. $H_{bulk}(ZnO)$ is the formation entropy of bulk ZnO calculated as 4.02 eV/ZnO in our calculations, which is compared to the experimental value of 3.63 eV [40] and the previous theoretical result of 3.94 eV [35].

3. Results and discussion

3.1. *Electronic properties of bulk ZnO*

Band structure and partial density of state (PDOS) of bulk ZnO have been calculated in our previous work [34]. Bulk ZnO is a direct band gap semiconductor and its band gap is 0.72 eV, which is larger than the theoretical result of X.D. Zhang et al. [41] (0.5 eV), but much smaller than the experimental value of 3.37 eV [42]. It is well known that the underestimated band gap is due to exchange-correlation energy. Fig. 2 gives the imaginary part $\varepsilon_2(\omega)$ of dielectric function of pure ZnO compared with the experimental values of Refs. [43] and [44]. $\varepsilon_2(\omega)$ of pure ZnO has two main peaks at 4.19 and 9.10 eV respectively. In this part, we have used the scissor operation, which is a kind of method that has been proved [45,46]. The scissors operator is a rigid shift and can describe the difference between the theoretical and experimental band gap values. When the experimental value is known, you can perform a band structure calculation by setting the scissors operator to the difference between the two values [47]. By GGA method, the calculated peak of 4.19 eV is due to optical transitions between O 2p states in the valence band maximum and Zn 4s states in the conduction band minimum. The peak of 9.10 eV is caused by optical transitions between Zn 3d states and O 2p states. The peaks are very close to the other first-principles estimations [41,48,49]. The above