Study on electronic structure and optical properties of doped ZnO system

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Abstract: In this paper, the electronic structure and photoelectric properties of P and Cu doped ZnO systems have been studied by Density functional theory method. The results show that the formation energies of ZnO-P-Cu, ZnO-P-2Cu, ZnO-P and ZnO-Cu systems decrease in turn compared with the intrinsic ZnO system, the ZnO-P, ZnO-P-Cu, ZnO-P-2Cu and ZnO-Cu systems have higher activity, the band gap of ZnO-P and ZnO-P-2Cu systems is reduced, and the electron transition is easier. In the doped system, the peak of the dielectric function shifts to the left and increases, the absorption of the electron to the photon increases obviously, and the absorption spectrum appears red shift, from the calculated results, it can be concluded that P and Cu single-doped and co-doped ZnO have great influence on the electronic structure and optical properties of ZnO system, which provides a theoretical basis for further study of the influence of doping on the properties of ZnO.

1. Introduction

As a new type of Indirect bandgap material, zinc oxide has attracted much attention in recent years due to its low dielectric constant, high photoelectric coupling rate, high chemical stability, excellent piezoelectric and photoelectric properties. The gap width of ZnO is 3.37 ev and the exciton binding energy is 60 meV. Compared with other photoelectric materials, ZnO has potential applications in many fields such as photoelectricity, ferromagnetism and thin film preparation. Researchers have been looking for ZnO products with good properties. The main methods are metal or non-metal doping, dye sensitization, noble metal deposition, and so on, the n-type semiconductor Zno has lower performance than p-type, so how to obtain high-performance p-type ZnO is the key to its wide application.

The electronic structure and optical properties of N-Mn doped ZnO have been studied. The results show that the optical Absorption Coefficient of N-Mn co-doped ZnO increases in the visible region, the electronic structure of Ag-N co-doped ZnO has been studied, and the results show that the acceptor energy level of Ag-N co-doped ZnO is shallower than that of single doped ZnO, and the localization of hole state is decreased, the Electron structure and optical properties of Ce-N co-doped ZnO have been studied.
Zno have been studied by Zhao can et al[10], and the results show that Ce-N co-doped ZnO is a kind of potential p-doped ZnO, the p-type conductivity of C-cu co-doped ZnO has been studied by Ding Luocheng et al[11]. The results show that p-type ZnO can be obtained in the doped system When the ratio of C-Cu to ZnO is 1:2, a new semiconductor material with higher p-type, better electron migration, better conductivity and lower doping energy can be obtained Xiao Lijuan et al[12] have studied the latest progress of p-type doped ZnO thin films, discussed the difficulties in the preparation of p-type ZnO thin films and their solutions, and reviewed the latest progress in the study of the first principles of P-Cu co-doped ZnO, there have been no reports of this.

The Crystal Structure, electronic structure and optical properties of P-Cu single-doped and co-doped ZnO have been studied by first-principles calculations, it is found that P-Cu doping exhibits better p-type characteristics and higher stability, which provides theoretical support for exploring the conduction mechanism of ZnO.

2. Method of calculation
The energy band structure, density of states and optical properties of P-doped, Cu-doped, P-Cu co-doped and P-2Cu co-doped ZnO systems have been calculated and analyzed. The lattice constants $a=b=3.2342\text{Å}, c=5.1901\text{Å}, \alpha=\beta=90^\circ, \gamma=120^\circ[13]$. The unit cell used in this paper is a 2x2x2 supercell based on a ZnO unit cell. When doping, P and Cu are used to replace the O and Zn sites in ZnO, respectively. The electron configurations of the co-doped system atoms are Zn(3d$^{10}$4s$^2$), O(2s$^2$2p$^4$), P(3s$^2$3p$^3$), Cu(3d$^{10}$4s$^1$). The calculation uses Materials. The CASTEP module in Studio 8.0 uses GGA/PBE exchange correlation functionals. The Brillouin zone integral uses 3x3x1 k-point settings, and the plane wave truncation energy formula is 340eV. The maximum displacement is 0.001Å, the internal stress is 0.05Gpa, and the intermolecular The maximum interaction force is 0.03 eV/Å, and the overall energy of the structure converges to 1.0x10$^{-5}$ ev/atom.

3. Results and Discussion
3.1. Formation Energy and stability analysis
Table 1 shows the lattice constants, volume and formation energy of the optimized systems of ZnO, ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu. The formation energy is the physical quantity which indicates the difficulty and stability of doping formation. The formula is:

$$E_f=E_{\text{ZnO-mP-nCu}}-E_{\text{ZnO}}-mE_P-nE_{\text{Cu}}+mE_{\text{O}}+nE_{\text{Zn}}$$

In the formula, $E_{\text{ZnO-mP-nCu}}$ represents the total energy of P and Cu doped system, $E_{\text{ZnO}}$ represents the total energy of Intrinsic System, $E_P$, $E_{\text{Cu}}$, $E_{\text{O}}$, $E_{\text{Zn}}$ represents the ground state energy of P, Cu, O and Zn atoms, respectively, $m$ and $n$ represent the number of doped and substituted atoms. Compared with ZnO, the defects in ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu can easily cause the change of crystal energy. The calculated results show that the cell volume and c value of ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu systems increase, except ZnO-P systems, the larger the c/a values, the smaller the lattice symmetry of ZnO, and the shift of the impurity energy level toward lower energy, which is favorable for the formation of shallow acceptors. The formation energy of ZnO-P and ZnO-Cu systems is lower than that of ZnO-P-Cu and ZnO-P-2Cu systems. The Formation Energy of ZnO-Cu system is the lowest, which indicates that the doped system is easier to form.

| Model               | $a=b$ (Å) | $c$ (Å) | $c/a$ | $V$ (Å$^3$) | $E_f$/eV |
|---------------------|-----------|---------|-------|-------------|----------|
| ZnO$^{\text{exp}[14]}$ | 6.498     | 10.412  | 1.602 | 439.636     | \        |
| ZnO                 | 6.585     | 10.597  | 1.609 | 397.997     | \        |
| ZnO-P               | 7.074     | 10.952  | 1.548 | 446.193     | 3.1389   |
| ZnO-Cu              | 6.588     | 10.617  | 1.612 | 397.536     | 1.7336   |
| ZnO-P-Cu            | 6.612     | 11.044  | 1.6702| 412.415     | 6.1154   |
| ZnO-P-2Cu           | 6.553     | 10.925  | 1.6672| 408.899     | 3.5019   |
3.2. Band Structure analysis

Fig.1 shows the energy band structure of ZnO system before and after doping. (a), (b), (c), (d) and (e) are ZnO, ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu system energy band, where G, F, Q and Z are high symmetry points in Brillouin zone, the band gap of ZnO-Cu system is 0.734 eV, 0.688 eV, 0.169 eV, 0.410 eV and 0.378 eV, respectively. The less energy is needed for stimulated transition of ZnO-Cu system, the system can respond to stimulated light even in low light energy environment. As can be seen from Fig.1(a), the energy band of ZnO is a typical Indirect bandgap structure, and the band gap of the system is similar to the calculated results in [15-16], but quite different from the experimental value of 3.37 eV[17]. The gap in band gap is mainly caused by GGA approximation, the excessive consideration of the electron-electron interaction leads to the expansion of the valence band and the conduction band, which reduces the band gap width, but this does not affect our analysis of the band gap variation.

As can be seen from Fig.1(b), the band gap of p-doped system decreases, and the coupling of P-3p and Zn-3d states is the main reason for the formation of p-type Degenerate semiconductor in the valence band of p-doped system, the energy required for electron to absorb light energy from fermi level to conduction band is minimum. As can be seen from figures 1(c), 1(d) and 1(e), different amounts of impurity energy levels are present in the doped band gap, and the number increases in turn, indicating that the carrier concentration is increasing, the results show that the activities of ZnO-P-Cu, ZnO-P-2Cu and ZnO-Cu systems are increased in turn.

3.3. Density of states analysis

The density of states of ZnO, ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu systems is given in Fig.2. It can be seen from Fig.2(a) that the valence band of ZnO is mainly formed by the hybridization of the 3d state of Zn and the 2p state of O, and the valence band top is mainly composed of the 2p state of O, the conduction band is mainly contributed by the 4s state of Zn. It can be seen from Fig.2(b) that the valence band of P-doped ZnO system is mainly contributed by the 3d state of Zn, the 2p state of O and the 3p state of P, the valence band top is formed by the hybridization of the 2p state of O and the 3p state orbit of P, and the conduction band bottom is mainly determined by the 4s state of Zn. It can be seen from Fig.2(c) that the valence band of Cu-doped ZnO system is mainly contributed by the 3d states of Cu and Zn, the valence band top is formed by the hybridization of the 2p states of O and the 3d states of Cu, and the conduction band bottom is mainly contributed by the 3d states of Cu. It can be seen from figures 2(c), 2(d) and 2(e) that the 3d state of Cu in ZnO-Cu and ZnO-P-Cu systems does...
not change much near Fermi level, and the 3d state of Cu in ZnO-P-2Cu system moves to the right with strong locality, the impurity energy levels in the band gap are mainly contributed by the 3d state of Cu. It can be seen that the Cu atoms have a great influence on the system, which enhances the localization of the system and results in the increase of the impurity energy levels in the forbidden band.

3.4. Optical properties

Fig. 4 shows the reflection Spectra (a), Absorption Spectra (b), dielectric function imaginary part (c) and loss function (d) of ZnO, ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu systems. As can be seen from Fig.3(a), the reflection peaks of the doped system shift to the left and the reflectivity decreases obviously below 18.2eV. In the calculated energy range, the reflectivity of ZnO-P, ZnO-Cu and ZnO-P-2Cu systems is obviously lower than 18.2 eV, which may be due to the decrease of the conductivity of ZnO films with the increase of P and Cu doping. As can be seen from Fig.3(B), the doping system shows an obvious red shift, which is caused by the decrease of the forbidden band width of the doped system. When the forbidden band width decreases, the more easily the electrons are excited from the valence band to the conduction band, the less energy the electrons need, this induces a red shift at the absorption edge. In doping system, the number of absorption peaks increases obviously, which indicates that the transition probability of Valence Band Electron Guide Band of excited state increases.

Fig.3(c) is the imaginary part of the dielectric function of the system. As a broad band gap, the spectrum of ZnO is produced by the electron transition between the energy levels. The dielectric peaks can be explained by the energy band structure and the density of states of ZnO Indirect bandgap. Compared with the Intrinsic ZnO, the main peaks of the imaginary part of the dielectric function of each doped system move to the low energy region, which is related to the decreasing of the forbidden band width, the lattice distortion and the formation of the impurity energy level. As can be seen from Fig.3(c), the peaks of ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu systems disappear around 1.77 eV, while the main dielectric peaks are formed at 1.70 eV, 0.27 eV, 0.31 eV and 0.36 eV at the low energy.
end, respectively, the large amplitude of dielectric peak in ZnO-P system is mainly due to the enhancement of electron transition between impurity level and conduction band due to the introduction of impurity level in the forbidden band. Fig. 3(d) is an energy loss spectrum. It can be seen from the diagram that the energy loss of pure zinc oxide is about 18eV, and the doping makes the energy loss peak move to the low energy end.

4. Conclusion

In this paper, the electronic structure and optical properties of P and Cu doped ZnO systems have been studied by using the first principles ultrasoft pseudopotential method of Density Functional theory and the Generalized Gradient Approximation method. The results show that the band gap of ZnO is 0.734 eV, the volume of ZnO-P, ZnO-Cu, ZnO-P-Cu and ZnO-P-2Cu systems is larger than that of ZnO, and the formation energy of doped systems decreases in turn, the activity of ZnO-P-Cu, ZnO-P-2Cu and ZnO-Cu systems increases in turn, the bandgap width of ZnO-Cu and ZnO-P-2Cu systems decreases, the energy of electron transition decreases, the electron transition occurs more easily, and the dielectric function peak of doped systems shifts to the left and increases, the absorption of Photon is obviously enhanced, and the absorption spectrum of doped system appears red shift. From the calculation results, it can be concluded that P, Cu and co-doped ZnO have great influence on the electronic structure and optical properties of the system.

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