First-principles study on electronic structure and optical properties of N-Fe co-doped ZnO

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Abstract: In this paper, the electronic structure and photo-electric properties of N and Fe co-doped ZnO systems have been studied by using Density functional theory method. The results show that the formation energy of ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems decreases in turn, the doping is easier to realize. Compared with the ZnO system, the activity of ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems increases in turn, the band gap of ZnO-N and ZnO-N-2Fe systems decreases, and the electron transition is easier in the doped system. The peak of the dielectric function shifts to the left, the absorption of the electron to the photon increases obviously, and the absorption spectrum appears red shift. It can be concluded that the electronic structure and optical properties of ZnO are greatly affected by the single and co-doping of N and Fe, which provides a theoretical basis for the further study.

1. Introduction

As a new type of Indirect bandgap material, zinc oxide (ZnO) has attracted much attention in recent years[1-3]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 60mev[4]. Compared with other photoelectric materials, ZnO has potential applications in many fields[5-7]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- and Mn-doped ZnO have been studied by Pang Guowang et al[8]. The results show that the Absorption Coefficient of N-Mn co-doped ZnO increases and the charge-binding ability of the system increases in the visible light region. The electronic structure of Ag-N co-doped ZnO has been studied[9]. The results show that the acceptor energy level of co-doped ZnO is shallower than that of single doped ZnO, and the localization of hole state is decreased, thus improving the conduction properties of p-type ZnO, the Electron structure and optical properties of Ce-N co-doped ZnO have been studied by Zhao can et al[10],...
the p-type conductivity of C-Cu co-doped ZnO has been studied by Ding Luocheng et al \cite{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 \cite{12} have studied the latest progress of p-type doped ZnO films, discussed the difficulties in the preparation of p-type ZnO films and their solutions, and reviewed the latest progress in the study of the first principles of N-Fe co-doped ZnO, there have been no reports of this. In this paper, the crystal structure, electronic structure and optical properties of N-Fe single-doped and co-doped ZnO systems have been studied by first-principles calculations, it is found that N-Fe co-doping exhibits better p-type characteristics and higher stability than the traditional single doping, which provides theoretical support for exploring the conduction mechanism of ZnO.

2. Method of calculation

In this paper, the models of N-doped, Fe-doped, N-Fe co-doped and N-2Fe co-doped ZnO systems have been constructed, and the energy band structure, density of states and optical properties of these systems have been calculated and analyzed. The hexagonal Wurtzite structure of ZnO is used in this paper. The Space Group of ZnO is P6\(_{3}\)mc, the lattice constant is \(a=b=3.2342\,\text{Å}, c=5.1901\,\text{Å}, \alpha=\beta=90^\circ, \gamma=120^\circ\)\cite{13}. The Crystal Cell is a 2x2x2 supercell based on the original cell of ZnO, fig. 1 shows the supercell structure of ZnO, ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-2Fe respectively. The electronic configurations of the doped system are Zn(3d\(^{10}\)4s\(^2\)), O(2s\(^2\)2p\(^4\)), N(2S\(^2\)2P\(^3\)) and Fe(3d\(^6\)4s\(^2\)), respectively. The calculation uses CASTEP module in Materials Studio 8.0, uses GGA/PBE to exchange correlation functional, Brillouin Integration is set at k point of 3x3x1, the plane wave truncation energy is 340eV, the maximum displacement is 0.001Å and the internal stress is 0.05Gpa, the maximum intermolecular force is 0.03eV/Å and the total energy of the system converges to 1.0x10\(^{-5}\) ev/atom.

![Fig.1 Supercell structure of ZnO, ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe](image)

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-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe. The formation energy is a physical quantity which indicates the difficulty and stability of doping formation. The formula is:

\[ E_f = E_{\text{ZnO}-mN-nFe} - E_{\text{ZnO}} - mE_N - nE_{Fe} + mE_O + nE_{Zn} \]  

In the formula, \(E_{\text{ZnO}-mN-nFe}\) represents the total energy of N, Fe doped system, \(E_{\text{ZnO}}\) represents the total energy of the Intrinsic System, \(E_N, E_{Fe}, E_O, E_{Zn}\) represents the ground state energy of N, Fe, O and Zn atoms respectively, \(m\) and \(n\) represent the number of atoms doped and substituted. Compared with the perfect ZnO crystal, the energy of the crystal is changed by the existence of various defects. The calculated results show that the cell volume, a value and c value of ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems increase compared with the ZnO system, the smaller c/a values, the smaller the lattice symmetry of ZnO, and the higher the impurity energy level, the easier the shallow acceptor to form. The formation energy of ZnO-N-Fe and ZnO-N-2Fe systems is lower than that of ZnO-N and ZnO-Fe systems. The formation energy of ZnO-N-2Fe system is the lowest, which indicates that ZnO-N-2Fe system is easier to form.
3.2. Band Structure analysis

Fig.2 shows the energy band structure of ZnO system before and after doping. (a), (b), (c), (d) and (e) are the energy band of ZnO, ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe, where G, F, Q and Z are the high symmetry points in Brillouin zone, the band gap of the system is 0.734 eV, 0.163 eV, 0.809 eV, 0.74 eV and 0.492 eV respectively. The smaller the band gap is, the smaller the energy is needed for the excited transition. Even in low light energy environment, the system can respond to light excitation. As can be seen from Fig.2(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\cite{15-16}, but quite different from the experimental value of 3.37 eV\cite{17}. The gap in band gap is mainly caused by GGA approximation, the excessive consideration of the interaction between the electrons leads to the expansion of the valence band and the conduction band, which reduces the band gap width. However, this phenomenon, which is common in theoretical calculations, does not affect the analysis of the band gap variation of the system.

3.3. Density of states analysis

The total and fractional densities of states of ZnO, ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems are given in Fig.3. As can be seen from Fig.3(a), the valence bands of ZnO are mainly formed by the hybridization of the 3d states of Zn and the 2p states of O, the top of Valence Band is mainly composed of O 2p state and the conduction band is mainly contributed by Zn 4s state. It can be seen from Fig.3(b) that the valence band of n-doped ZnO system is mainly contributed by the 3d state of Zn, the 2p state of O and the 2p state orbit of N, and the bottom of conduction band is mainly determined by the 4s state of Zn. It can be seen from Fig.3(c) that the valence band of Fe-doped ZnO system is
mainly contributed by the 3d states of Fe and Zn, the valence band top is formed by the hybridization of the 2p states of O and the 3d states of Fe, and the conduction band bottom is mainly contributed by the 3d states of Fe. Comparing with ZnO-Fe system, it can be seen from figures 3(d) and 3(d) that the 3d state of Fe in ZnO-Fe and ZnO-N-Fe systems moves to the vicinity of Fermi energy level, and the impurity energy level in the forbidden band is mainly contributed by the 3d state of Fe. It can be seen that N and Fe atoms in the co-doped system influence each other greatly, which enhances the localization of each other and leads to an increase in the number of impurity energy levels in the forbidden band compared with that in the Fe single doped system.

3.4. Optical properties

The Reflection Spectra(a), Absorption Spectra(b), Imaginary part of Dielectric Function(c) and Loss Function(d) of ZnO, ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems are given in Fig.4. As can be seen from Fig.4(a), the reflection peaks of the doped system shift to the left and the reflectivity decreases gradually after the frequency is 17.5eV. Compared with ZnO system, ZnO-N-Fe and ZnO-N-2Fe systems have lower reflectivity in the near-ultraviolet region in the calculated energy range, which may be due to the decrease of the conductivity of ZnO films with the increase of N and Fe doping. As can be seen from Fig.4(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 electrons are more easily excited from the valence band to the conduction band, and the required electron energy is reduced, thus, the red-shift phenomenon occurred at the edge of absorption spectrum. In doping system, the number of absorption peaks increases obviously, which indicates that the transition probability of valence-band Electron guide-band in excited state increases. Fig.4(c) is the imaginary part of the dielectric function of the system. The imaginary part of the dielectric function is closely related to the stimulated transition of the electrons between the energy levels. The larger the number of the imaginary part, the greater the probability of the electron absorbing photons and the number of the electrons in the excited state, the greater the probability of the next transition. At the same time, ZnO acts as a broad band gap, and its Spectra are produced by electron transitions between energy levels. The dielectric peaks can be explained by the energy band structure and the density of states of ZnO. 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.4(c), the peak of ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems around 1.77eV is lost compared with ZnO system, the ZnO-Fe system has four main dielectric peaks at 0.28eV, 0.36eV, 0.83eV and 0.28eV respectively, this is mainly due to the enhancement of electron transition between impurity levels or between impurity levels and conduction bands due to the introduction of impurity levels in the forbidden band. Fig.4(d) is an energy loss spectrum. As can be seen from the diagram, their energy loss is very small. The loss peak of pure zinc oxide is about 18eV. The doping makes the energy loss peak move to the low energy end.
4 Conclusion
In this paper, the first principles ultrasoft pseudopotential method of the Density functional theory are used to study the electronic structure and photoelectric properties of N, Fe single doped and codoped ZnO system. The results show that the band gap of ZnO is 0.734 eV, and the volume of ZnO-N, ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems are larger than ZnO. The formation energy of doped system decreases in turn, and the doping can be realized more easily. Compared with the ZnO system, the ZnO-Fe, ZnO-N-Fe and ZnO-N-2Fe systems have higher activity, lower band gap width and lower electron transition energy for ZnO-N and ZnO-N-2Fe systems, the higher the electron transition, the higher the left shift of the dielectric function peak, the stronger the electron absorption, and the red shift of the Absorption Spectra, the results show that the electronic structure and optical properties of the system are greatly influenced by N, Fe and co-doped ZnO.

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