The electronic structure, density of states and optical properties of ZnO doped by Mg in substitutional and interstitial position

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Abstract. The formation energy, electronic structure, density of states and optical properties of ZnO doped by Mg in substitutional and interstitial positions are studied. It is found that the band gap of ZnO is enlarged by doping Mg in the substitutional position, and the ZnO doped by interstitial Mg becomes n-type semiconductor. The optical properties of pure ZnO and ZnO doped by Mg in substitutional position differ little. However, the difference between the optical properties of pure ZnO and ZnO doped by Mg in interstitial position is obvious. Doping ZnO with Mg in interstitial position, the absorption edge shows blue shift, the refractive index decreases, and the light permeability in the energy range from visible to near ultraviolet (0-4.2eV) gets better. Our research may provide helpful reference to the developments of ultraviolet optoelectronic devices.

Introduction

ZnO is a kind of typical direct-band-gap semiconductor for optoelectronic applications with large band gap (3.37eV) under room temperature, and its exciton binding energy is about 60meV [1]. ZnO also has other attractive features, such as environmental friendship and low cost etc [2]. It's found by experimenters that the electronic and optical properties of ZnO can be tuned by changing the doping content of Mg. At present, ZnMgO is a hot research topic in ultraviolet photoelectric devices.

First principles calculation is a well known effective theoretical method to study the physical properties of semiconductors. There emerge a great number of articles in first-principles calculations, which reported the variations of structural, electronic and optical properties of ZnO with the doping content of Mg [3]. These works shed little light on the Mg doping behavior and the physical properties of ZnMgO systems. However, in almost all the theoretical models considered, the Mg is in the substitutional position (Mg_S) of Zn, and the calculations based on the models with Mg in the interstitial positions (Mg_I) are seldom seen. But experimenters can always find some clues, which indicate that

whatever the Mg doping content is, there perhaps is a small part of Mg atoms existing in the interstitial positions in the samples of ZnMgO [4]. Furthermore, Mg_I is found to be able to greatly influence the lattice parameters and physical properties of the system. This paper calculated the formation energy, electronic structure and optical properties of wurtzite ZnO doped by Mg_S and Mg_I by first principle calculations. We further analyzed the optical constants of the two systems and compared them with that of pure ZnO.

Methods and models

The calculations are performed with the CASTEP code [5]. We use the generalized gradient approximation in the Perdew-Burke-Eruzerhof scheme. The maximum plane-wave cutoff is taken to be 550 eV. Both the parameters of the unit cell and the internal coordinates of the atoms are fully relaxed until forces have converged to less than 1×10^{-6} eV/Å and all the stress components are less than 0.1 kbar. In the calculations of the optical properties, we use the scissor operations. The $3\times3\times2$ supercell containing 72 atoms is adopted for pure ZnO, as shown in Fig. 1. Gray, red and green spheres represent Zn, O and Mg atoms, respectively. The symbol "I" and "S" in Fig.1 represent the interstitial position and substitutional position, respectively.

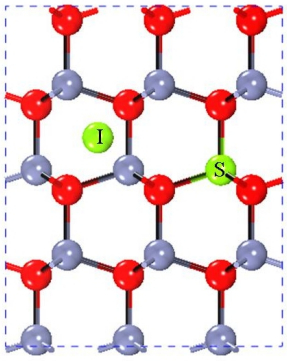

Figure 1. The $3\times3\times2$ wurtzite ZnO supercells (side view) doped by Mg in different positions.

Calculation and results

Formation energy

Traditional $Mg_xZn_{1-x}O$ models all include no Mg_I in the wurtzite supercell. In order to see whether Mg_I can exist, we calculated the defect formation energy of wurtzite $Zn_{36}Mg_1O_{36}$ (Mg_I) and $Zn_{35}Mg_1O_{36}$ (Mg_S). The defect formation energy is defined as

$$E_f = E(defect) - E(perfect) - \sum n_i m_i \quad (1)$$

Here, E_f represent the defect formation energy, $E(defect)$ represent the total energy of the system containing the defect, $E(perfect)$ represent the total energy of the perfect system, n_i is the number of

the ith atom added (negative) or reduced (positive) to the system, and m_i is the chemical potential of the ith metal atom (Mg or Zn). It's found that the defect formation energies of the $3\times3\times2$ ZnO supercells containing single Mg_S or Mg_I are -2.8 eV and -0.78 eV, respectively. Negative values of defect formation energy mean that both the systems are possible to form, however, the Mg in substitutional position is more stable than that in interstitial position. Our calculation result is in agreement with that reported in previous reference [6].

Electronic structure and density of states

The energy band of pure ZnO and ZnO doped by Mg_S or Mg_I are calculated. For pure ZnO, the maximum of valence band (VBM) is mainly contributed by O 2p states, and the minimum of conduction band (CBM) is determined by Zn 4s states. It's found that the conduction band of ZnO material shifts slightly toward high energy region and its band gap increases a little when it's doped by Mg_S. The Fermi level shifts toward high energy region and comes into the conduction band when it's doped by Mg_I. It's obvious that this is caused by the increase of the number of electrons in the ZnO when doped by Mg_I. The minimum energy band gap of pure ZnO, ZnO doped by Mg_S and Mg_I are 0.92, 0.97 and 0.75eV, respectively. In order to analyze the influences of Mg-doping in different doping positions on electronic properties, we calculated the total and partial density of states (TDOS and PDOS) of these three models. It is easy to find that Mg 2s and Mg 2p states emerge in the valence band and conduction band of ZnO doped by Mg_S (shown in Fig. 2(a)). The PDOS of Zn and O atoms have little difference from that of pure ZnO. The CBM shifts toward high energy region when the Zn is substituted by the Mg atom. Therefore, the band gap of ZnO doped by Mg_S is broader than that of pure ZnO. It's also found that there exist three differences between the PDOS of Mg and Zn atoms. First, the minimum energy positions of Mg 2p states and Zn 3p states in the conduction band is higher than that of Zn 4s states by about 1 eV. Second, the peak strength of the Zn 4s states is about three times that of the Mg 2s states in the energy range of (-4.5, -2.5)eV. Third, the peak strength of the Zn 3d states between -10 and -7.5 eV is much stronger than that of Mg 2s and 2p states. These results are caused by the differences of the radius and electronegativity between the Mg and Zn atoms.

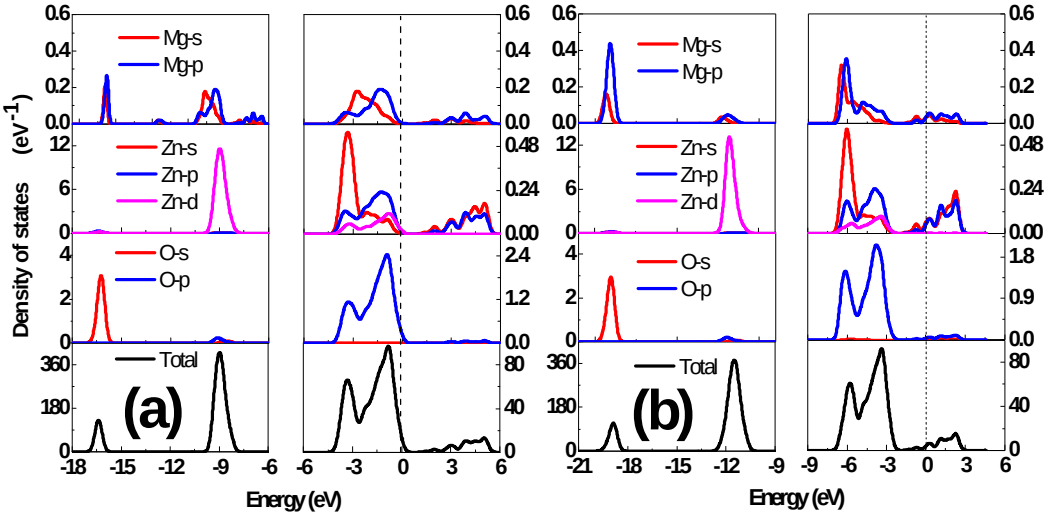

Figure 2. TDOS and PDOS of the ZnO doped by Mg_S (a) and Mg_I (b).

Fig. 2(b) shows the TDOS and PDOS of ZnO doped by Mg_I. It can be found that the Fermi level emerges in the conduction band, which is due to the increase of electrons induced by the Mg_I atoms. Three differences can be easily found from Fig. 2(b). First, the strength of Mg_I 2p states in low energy region is stronger than that of the Mg_S. Second, in valence band, the energy positions of the Mg_I 2s and 2p peaks are different from that of the Mg_S, and the strength of the former is stronger than the latter. Third, the peak closest to the CBM of 2s states of Mg_I is more close to the VBM than that of the Mg_S. These differences are caused by their different surrounding conditions of the Mg atoms.

Optical properties

The optical properties of a medium can be described by the complex dielectric response function as $e(w) = e_1(w) + ie_2(w)$. The $e_2(w)$ can be calculated from the matrix elements of the wave function for occupied and non-occupied states. The other optical parameters, such as the absorption coefficient et al, can be obtained from $e_1(w)$ and $e_2(w)$. Dielectric function is the pandect of the optical properties for any materials, so we first calculate and plot them in Fig. 3. It's found that there are little difference between the dielectric spectrums of pure ZnO and ZnO doped by Mg_S. However, the dielectric spectrum of ZnO doped by Mg_I is obviously different. First, the response edge in the low energy region has a blue shift (about 2 eV) relative to that of the two other cases. Second, their numbers of dielectric peaks do not equal. Third, the strengths of their main peaks differ a little. The dielectric spectrum is related with the absorption coefficient. The peaks of dielectric spectrum can be explained by the transitions between the peaks in the DOS. The first dielectric peak corresponds to the transitions between the VBM and CBM. Fig. 3 shows that the first dielectric peak of ZnO doped by Mg_S is weaker than that of the pure ZnO, but the energy position of the former is slightly higher than that of the latter. This is because that the strength of the total PDOS peak of Zn 4s decreases and the peaks show slight blue shift in case of ZnO doped by Mg_S. The second peak corresponds to the

transitions between the Zn 3d states and O 2p states in the valence band. The second peak of ZnO doped by Mg_I shift toward high energy region by about 0.2 eV relative to that of pure ZnO.

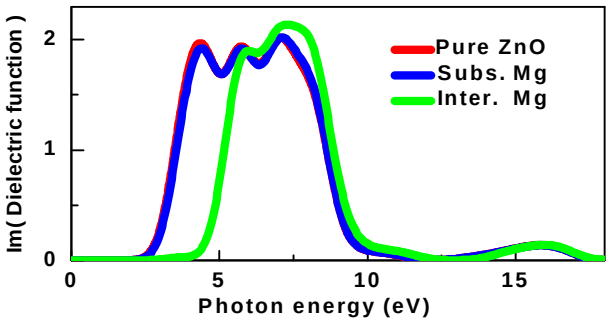

Figure 3. Imaginary part of dielectric functions of the three types of ZnO materials.

The absorption coefficient of material represents the percentage of light intensity attenuation when light propagates unit distance in the medium. The absorption coefficients of pure ZnO and ZnO doped by Mg_S equal to zero in the energy range (0-1.5 eV), and they remain small in the near ultraviolet range (1.7-3.1 eV). The absorption coefficients of ZnO doped by Mg_I equal to zero in the energy range (0-1.56 eV), and they remain small in the near ultraviolet range (1.7-4.2 eV). The reflectivity and extinction coefficients in the visible and near ultraviolet range almost equals to zero, they are by far smaller than that of the pure ZnO and ZnO doped by Mg_S. Therefore, it can be concluded that the transmittance of ZnO doped by Mg_I is better than that of the other two kinds of materials.

Conclusions

The band gap of ZnO doped by Mg_S is larger than that of pure ZnO. The ZnO doped by Mg_I becomes n-type semiconductor. The optical properties of ZnO doped by Mg_I are obviously different from those of pure ZnO and ZnO doped by Mg_S. The transmittance of ZnO doped by Mg_I in the energy range of visible to near-ultraviolet is obviously high. The doping of Mg_I can cause the blue shift of absorption edge and decrease of refractive index. ZnO doped by Mg_I has special optical properties, which may be used in future development and design of optoelectronic devices.

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