First-principles study on electronic and optical properties of Mg-N dual-acceptor codoped CuAlO2

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Keywords: Mg–N codoped CuAlO2, electronic structures, optical properties, first-principles

Abstract

Incorporation of impurities in CuAlO2 provides an opportunities to modulate its electronic and optical properties, which can be exploited for the applications of optoelectronic devices. Among the various elements doped of CuAlO2, research on the codoping magnesium (Mg) with nitrogen (N) which may be a promising way for fabricating p-type CuAlO2 is still limited. Here, the first-principles calculation based on density functional theory was used to investigate the electronic and optical properties of Mg-doped, N-doped and Mg–N codoped CuAlO2. Compared with the undoped CuAlO2, the lattice parameters a and c of the Mg–N codoped CuAlO2 become larger and smaller, respectively. The acceptor level induced by 2p state of Mg in N-doped CuAlO2 is very deep. The undoped and Mg-doped CuAlO2 has indirect band gap. Whether the deep acceptor level or the indirect band gap, it is unfavorable to p-type doping or light emission. Due to the hybridization of 3p state of Mg and 2p state of N on the top of the valence band, the Mg–N codoped CuAlO2 not only has a direct band gap, but also has a shallower acceptor level (about 0.24 eV above the top of the valence band). The optical properties of CuAlO2 changes obviously after Mg–N codoping in the area of low energy. These results suggest that the possibility of enhancing the hole concentration in CuAlO2 by Mg–N dual-acceptor codoping which will be beneficial to the application of CuAlO2 in optoelectronic devices.

1. Introduction

Transparent conducting oxides (TCOs) with wide band gap, high electrical conductivity and high optical transmittance in the visible light range have widely used in the light emission diodes, photovoltaic devices, transistors, gas sensor, catalysts, and so on [1–6]. Although n-type semiconductors have been widely used and developed, p-type TCOs are very few. The conductivity of p-type TCOs is usually 3–4 orders of magnitude lower than that of n-type TCOs, which largely limits the further application of TCOs in p–n junction device and transparent devices. The low conductivity of the p-type metal oxide semiconductor can be attributed to the metal–oxygen bonding with strong ionic nature. The holes are localized at the top of the valence band (VB) dominated by the level of 2p state of O leading to a low conductivity [7].

In order to solve the dilemma of p-type TCOs materials, based on the theory of valence band chemical modification, in 1997 Kawazoe et al [8] have found that the ternary oxide with delafossite structure (A B5+ O2) is more suitably (A+ = Ag+, Cu+, Pt+, Pd+, B5+ = Al3+, Cr3+, Fe3+, Co3+, Ga3+, Y3+, Nd3+, La3+, In3+, and so on.). Meanwhile, they obtain p-type CuAlO2 with conductivity of 1 S cm−1 and band gap of 3.5 eV for the first time. The holes in undoped CuAlO2 mainly come from the intrinsic defects of copper vacancies (V Cu) and oxygen interstitials (Oi). The first-principles calculation also show that the acceptor energy levels of V Cu and Oi are very deep [9, 10]. Therefore, the undoped CuAlO2 has low hole concentration and conductivity. Many methods for obtaining high conductivity of p-type CuAlO2 have been done [11–20], such as peroxidation, controlling of annealing atmosphere or temperature, acceptor doping, and so on. Among them, the method of
acceptor doping is an effective way, such as Mg, Sb, N, Na, Ni, Fe, Ag doping et al [14–21]. However, due to the deep impurity level, low solubility and compensation by native defects, semiconductors with wide band gap have difficulty in doping for p-type with high conductivity. Due to the low doping concentration of acceptor and the mismatch of ion radius between the doping atom and the host atom, the p-type CuAlO2 still fails to meet the requirements of the optoelectronic devices based on p-n junctions. Due to the low solid solubility, the doping concentration of acceptor is limited due to the doping with single acceptor element. Recently, codoping has been widely used in semiconductor doping and has achieved good results, such as ZnO, ZnS, ZnSe, CuAlO2, GaN, AlN, Cr2O3, and so on [22–27]. Therefore, double acceptor codoping may be an effective way to enhance the doping concentration of acceptor which can be further increases the conductivity. It is well known that Mg and N has similar electronegativity and atomic radius to Al and O, respectively. The first-principles calculations and experiments also show that both Mg substitute Al and N substitute O play a role as acceptor in CuAlO2 [28–30]. Therefore, Mg–N codoping may be an effective way for p-type doping in CuAlO2.

However, there is no systematic theoretical and experimental study on the Mg–N codoped CuAlO2. Therefore, in this work, the band structures, density of states and optical properties of Mg–N codoped CuAlO2 were systematic investigated by the first-principles pseudo-potential method based on density functional theory (DFT) by using CASTEP code. In addition, as a comparison, the band structures, density of states and optical properties of undoped, N-doped and Mg-doped CuAlO2 were also calculated.

2. Computational details

The CuAlO2 delafossite structure has a rhombohedral symmetry with the space group of R3m [7]. In such structure, O–Cu–O dumbbells structure parallel to c-axis are formed by linearly coordinating between one Cu atom and two O atoms. Each Al atom and six O atoms form an octahedron. AlO2 layers was formed with Al-centered octahedra, which lie parallel to ab plane. In this work, the 2 × 3 × 1 CuAlO2 supercell with 72 atoms were constructed with initial lattice parameters of a = b = 2.858 Å and c = 16.958 Å [31]. The N-doped and Mg-doped CuAlO2 supercell were obtained by replace one O atom with N atom and one Al atom with Mg atom, respectively. The Mg–N codoped CuAlO2 supercell was obtained by simultaneously substituting one O atom with one N atom and one adjacent Al atom with one Mg atom. Mg can replace Al to form p-type doping and can also replace Cu to form n-type doping. However, it can be seen from the existing theories and experiments [15, 29], the formation energy of Mg substituted Al is the lowest, and Mg doping can enhance the conductivity of p-type CuAlO2. Therefore, it is feasible to only consider the substitution of Mg for Al without affecting the calculation results. The undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO2 supercells are shown in figures 1(a)–(d). The doping concentrations of Mg and N are 5.6% and 2.78%, respectively. In order to find the most stability Mg–N codoped CuAlO2 structures, the formation energies of Mg–N configuration with N being 1st, 2nd and 3rd nearest neighbor (NN) to Mg were calculated.

In this work, the calculations were performed based on density functional theory (DFT) by using the CASTEP package with a plane-wave basis set and ultra-soft pseudopotentials. The exchange-correlation functional was treated with the Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA). However, DFT with standard GGA underestimates the semiconductor band gap [28, 32]. Therefore, the generalized gradient approximation plus orbital potential (GGA + U) is a method commonly used to modify the calculated band gap [31–33]. Considering the correlation effect of Cu-3d orbit, U with 8 eV is set to Cu-3d orbit [31]. The valence electron configurations of Cu, Al, Mg and O atoms are Cu 3p63d6, Al 3s23p1, Mg 2p63s23p1, O 2s22p4, and N 2s22p6, respectively. Plane waves have been included up to a cutoff energy of 400 eV. 3 × 2 × 2 Monkhorst-Pack grids were used for integration within the Brillouin zone specific k-points. The energy calculation was carried out in the reciprocal space. The force and convergence criteria for energy were set to 0.03 eV Å−1 and 1 × 10−6 eV atom−1, respectively. The maximum tolerances of the stress and displacement were set to 0.05 GPa and 0.001 Å, respectively. The calculation and investigation of the band structures, total density of states (TDOS), partial density of states (PDOS), and optical properties were performed after optimization of geometry.

3. Results and discussion

3.1. Structural properties

In order to study the stability of the crystal structure, formation energies of the undoped, N-doped, Mg-doped and Mg–N codoped CuAlO2 were calculated by following equation [34]:

\[
\Delta E_{\text{form}} = E_{\text{total}} - \left( \sum E_{\text{atom}} + E_{\text{config}} + E_{\text{strain}} \right)
\]
Where $E_{\text{total}}^{m_{\text{CuAl}_2\text{MgO}_2\cdot2\text{N}}}$ is the total energy of doped CuAlO$_2$, $E_{\text{Cu}}^{\text{crystal}}$, $E_{\text{Al}}^{\text{crystal}}$, and $E_{\text{Mg}}^{\text{crystal}}$ are the energies of Cu, Al, and Mg at most stable phases, $E_{\text{gas}}^{\text{O}_2}$ and $E_{\text{gas}}^{\text{N}_2}$ are the energy of O$_2$ and N$_2$ molecular gas. $x$ and $y$ was the doped concentration of Mg and N in CuAlO$_2$, respectively. $m$ is 18 for the CuAlO$_2$ supercell with 72 atoms.

The formation energy can be used to characterize the stability of supercells. The lower the formation energy, the more stable the supercell. The formation energies of Mg–N configuration with N being 1st, 2nd and 3rd nearest neighbor to Mg were about $-3.162$, $-3.159$, and $-3.157$ eV atom$^{-1}$, respectively. It can be found that the Mg–N configuration with 1st nearest neighbor is the most stable. Therefore, only the Mg–N configuration with 1st nearest neighbor was considered in the following discussion about the Mg–N codoped CuAlO$_2$. Figure 2 shows the formation energy of the undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO$_2$ supercells. The formation energies of undoped, N-doped, Mg-doped and Mg–N codoped CuAlO$_2$ systems are $-3.211$, $-3.199$, $-3.170$, and $-3.162$ eV atom$^{-1}$, respectively. It can be found that the formation energy of the CuAlO$_2$ after doping becomes larger, indicating that the stability of the CuAlO$_2$ after doping becomes worse than that of the undoped CuAlO$_2$. From Figure 2, we can also found that the formation energy of the Mg–N codoped CuAlO$_2$ is the largest, which shows that the stability is worse than that of the undoped, N-doped and Mg-doped CuAlO$_2$. From the bond length of Cu–N (1.799 Å), Al–O (1.873 Å), Mg–O (2.249 Å), and Al–N (1.984 Å) in the Mg–N codoped CuAlO$_2$ supercells, it can be found that the codoping results in a large change in the lattice parameters.

Figure 1. Crystal structure of (a) undoped, (b) N-doped, (c) Mg-doped, Mg–N codoped CuAlO$_2$ with Mg–N configuration of (d) 1st NN, (e) 2nd NN, and (f) 3rd NN. (The brown, purple and red balls are copper, aluminum and oxygen atoms, respectively. The blue and green ball are nitrogen and magnesium atom, respectively.)
comparing with that of undoped CuAlO₂. Although the formation energy of the doped CuAlO₂ is higher than that of the undoped CuAlO₂, they are all negative, indicating that all the doped CuAlO₂ supercell are still stable.

Based on the setting parameters, the equilibrium structures of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂ were obtained by minimizing the forces and total energy based on CASTEP code. The calculation results of the optimized geometry of CuAlO₂ supercells before and after doping are shown in figure 3. The optimized lattice parameters $a$ and $c$ for the undoped CuAlO₂ are 2.883 Å and 17.223 Å, respectively, which are close to the theoretical and experimental results [31, 35], indicating that the theoretical calculation results based on these structure are reasonable and reliable. The lattice parameters (both $a$ and $c$) and volume of N-doped CuAlO₂ supercell show increase after the doping of N, which can be attributed to the N having a large ionic radius (1.45 Å) than that of O (1.32 Å). From Table 1, the length of Cu–N (1.917 Å) and Al–N (1.946 Å) bonds formed in nitrogen doped supercell are larger than that of Cu–O (1.905 Å) and Al–O (1.924 Å) bonds in undoped CuAlO₂ supercells, resulting in the increase of supercell volume. Compared with the undoped CuAlO₂, the lattice parameter $a$ for Mg-doped CuAlO₂ supercells show increased, while the lattice parameter $c$ show decreased. The length of Cu–O (1.893 Å) bond formed in Mg-doped CuAlO₂ is smaller than that of Cu–O (1.905 Å) bond formed in undoped CuAlO₂, while the length of Mg–O (2.046 Å) bond is larger than that of Al–O (1.924 Å) bond formed in undoped CuAlO₂. It can be found from the supercell geometry that the bonding direction of Cu–O and Cu–N bonds is along the $c$-axis, while that of Al–N, Mg–O, and Al–O bonds is in the $ab$ plane which perpendicular to the $c$-axis. Therefore, Cu–O and Cu–N bonds have great effect on the lattice parameter $c$, while Al–N, Mg–O and Al–O bonds have great effect on the lattice parameter $a$. As a result, the lattice parameters $a$ and $c$ of CuAlO₂ supercells show increase and decrease after Mg doping, respectively. Due to the ionic radius Mg (0.72 Å) is larger than that of Al (0.54 Å), the volume of Mg-doped CuAlO₂ show increases obviously. Considering the length of Cu–N (1.799 Å), Cu–O (1.898 Å), Mg–N (2.249 Å), Mg–O (2.026 Å), Al–N (1.978 Å), and Al–O (1.924 Å) bonds in Mg–N codoped CuAlO₂, the lattice parameters ($a$ and $c$) and volume for

Figure 2. Formation energy and band gap of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂ with 1st nearest neighbor Mg–N configuration.

Figure 3. Optimized lattice constants and volume of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂.
Mg–N codoped CuAlO₂ are between that of Mg-doped and N-doped CuAlO₂, as shown in figure 3. The volume change caused by Mg–N codoping is lower than that of by Mg doping. Therefore, the influence of Mg–N codoping on the structure is relatively small, which is conducive to reduce the influence of high doping concentration on the crystal structure and obtain high crystallization quality of CuAlO₂ with p-type conductivity.

Table 1 also show the overlap populations of electronic cloud between the atoms in undoped, N-doped, Mg-doped and Mg–N codoped CuAlO₂ calculated by using the Mulliken population analysis. The positive and negative values of overlap populations represent bonding and antibonding, respectively. A high overlap populations indicates a high degree of covalency in the bond [36]. Compared with the undoped CuAlO₂, the Cu–O bond in Mg-doped and Mg–N codoped has a smaller bond length and a larger overlap populations, indicating that enhanced covalent nature between Cu and O atoms. At the same time, it can be also found that the Cu–N bond in Mg–N codoped CuAlO₂ has a smaller bond length and a larger overlap populations comparing with that of in N-doped CuAlO₂, which indicates that the Mg–N codoping can further increases the covalent nature between Cu and N atoms. It is well known that strong covalent bond and weak ionic bond are favorable for p-type doping [34]. Better covalent hybridizations are conducive to hole delocalization. Therefore, it can be concluded that Mg–N codoping is an effective way for p-type doping for CuAlO₂.

### 3.2. Electronic properties

Doping with different atoms in the supercell will cause lattice distortion and impurity level, the valence band (VB) and conduction band (CB) edge can be changed. Figure 4 shows the band structure of undoped, N-doped, Mg-doped and Mg–N codoped CuAlO₂. The green line between the valence band and the conduction band represents the impurity level formed after doping. The Fermi level Ef is set at 0 eV and indicated by horizontal red dotted line in figure 4. The band gap of undoped CuAlO₂ is 2.641 eV, which is underestimated but more close to the experimental value of 2.99 eV [37]. Underestimate of the band gap is caused by the GGA approximation method. In this work only discusses the changes before and after doping, so this error does not affect the discussion of the results. The band gaps of N-doped, Mg-doped and Mg–N codoped CuAlO₂ are 2.471 eV, 2.561 eV and 2.537 eV, respectively, which are smaller than that of undoped CuAlO₂. Figures 4(a) and (c) shows the band structure of undoped and Mg-doped CuAlO₂. The indirect band gap of undoped CuAlO₂ is consistent with other theoretical calculation results [9, 31, 35]. After Mg doping, the energy level near the top of the valence band becomes relatively flat, but the minimum value of the conduction band is located at the G point, while the maximum value of the valence band is in the F-G direction, indicating that the Mg-doped CuAlO₂ is still an indirect band gap semiconductor. This indirect band gap characteristics will lead to poor light emission properties and have a great impact on the performance of the device. Figures 4(b) and (d) show the band structure of N-doped and Mg–N codoped CuAlO₂, it can be found that the maximum value of VB and the minimum value of CB are located at the same G point, indicating that they are all direct band gap semiconductor which will lead to better light emission properties.

After N doping, the bottom of the CB moves down to the direction of low energy, while the VB changes little, which leads to the decrease of the band gap of N-doped CuAlO₂. However, the changes of CB and VB of the Mg-doped and Mg–N codoped CuAlO₂ is smaller, which leads to a smaller change in band gap. The band gap of the Mg-doped and Mg–N codoped CuAlO₂ is smaller than that of undoped CuAlO₂ due to doping. From figure 4(b), it can be found that the acceptor energy level induced by N doping in N-doped CuAlO₂ is deep, which is unfavorable for obtaining CuAlO₂ with high hole concentration. Although a shallow acceptor energy level is formed at the top of the VB after Mg doping, as shown in figure 4(c), it can be seen that the top of the valence band and the bottom of the conduction band are not in the same position in the momentum space. Although the difference of the top energy levels of the valence band is small at different positions in the momentum space, Mg doped CuAlO₂ has the characteristics of indirect band gap which is unfavorable for
luminescence. For Mg–N codoped CuAlO₂, as shown in figure 4(d), it can be found that not only the band gap change to direct band gap after codoping with Mg and N, but also a shallow acceptor energy level is formed above the top of the VB about 0.24 eV, which is conducive to acceptor ionization, thus increasing the hole concentration. Therefore, the Mg and N codoping is an effective way to improve the acceptor ionization and light emission properties of CuAlO₂.

In order to further understand the variation in band gap and electronic structure, figure 5 shows the TDOS and PDOS of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂. The Fermi level E_F is set at 0 eV and indicated by vertical blue dash line in all DOS figures. From figure 5(a), it can be seen from that the VB of undoped CuAlO₂ mainly consists of the 2p orbit of O and 3d orbit of Cu which lead to p–d coupling, and the CB mainly consists of 3p orbit of Cu and 2p orbit of O. For N-doped CuAlO₂, N enters into the lattice and replaces O atom forming N–Cu–O bond, resulting in the change of band structure. After N doping, the 2p orbital of N, 2p orbital of O, and 3d orbital of Cu are hybridized to form VB. The CB mainly consists of 3p orbit of Cu and 2p orbit of O. As shown in figure 5(b), an acceptor energy level locate at about 0.72 eV above the E_F was induced by 2p orbital of N. The energy band locate at 12–15 eV can be attributed to the 2s orbital of N. For Mg-doped CuAlO₂, as shown in figure 5(c), Fermi level goes through the acceptor energy level formed by the 2p orbit of Mg. The acceptor energy level is located at about 0.19 eV above the E_F, indicating that a shallow acceptor energy level is formed above the top of the VB which will be favorable for p-type doping of CuAlO₂. For Mg-doped CuAlO₂, the VB is mainly composed of 2p orbit of Mg, 3d orbit of Cu, and 2p orbit of O, while the CB is still composed of 3p orbit of Cu and 2p orbit of O. Therefore, The 2p orbit of Mg contributes mainly to VB and little to the CB. For Mg–N codoped CuAlO₂, the PDOS of 3p state of Mg overlaps with that of 2p state of N, which leads to strong hybridization effect and forms a shallow acceptor level locate at about 0.24 eV above the top of the VB, as shown in figure 5(d). Due to the strong hybridization effect of 2p orbit of Mg and 2p orbit of N, the PDOS of 2p orbit of N moves to the area of low energy, resulting in the band gap of Mg–N codoped CuAlO₂ is larger than that of N-doped CuAlO₂. These results are consistent with the calculation results of band structure.

3.3. Optical properties
The complex dielectric function not only reflects the relationship between band structures and optical properties, but also helps to characterize the optical properties of crystals. The complex dielectric function can be expressed as [38]:

$$
\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 - (i\omega\tau)^{2}}
$$
Based on the real part $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$ of the dielectric constant, the absorption coefficient $\alpha(\omega)$, the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the reflectivity $R(\omega)$ and the energy loss function $L(\omega)$ can be calculated as following [38]:

$$
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)
$$

$$(2)$$

$$
\alpha(\omega) = 2\omega \sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}{2}}^{1/2}
$$

$$(3)$$

$$
n(\omega) = \sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) + \varepsilon_1(\omega)}{2}}^{1/2}
$$

$$(4)$$

$$
k(\omega) = \sqrt{\frac{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega)}{2}}^{1/2}
$$

$$(5)$$

Figure 5. Total density of states and partial density of states of (a) undoped, (b) N-doped, (c) Mg-doped, and (d) Mg–N codoped CuAlO$_2$. 
The imaginary part of the dielectric function of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO$_2$ are shown in figure 6. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ can be used to characterize the property of electron transport in materials. For undoped CuAlO$_2$, only one dielectric peak at 4.513 eV is observed, which can be attributed to the electron transition from 3d state of Cu and 2p state of O to 3p state of Cu. For N-doped, Mg-doped and Mg–N codoped CuAlO$_2$, besides the dielectric peak locate at about 4.5 eV, a new dielectric peak is observed at 0.910, 0.178, and 0.057 eV in the area of low energy, respectively. The new dielectric peaks of N-doped and Mg-doped CuAlO$_2$ can be attributed to the transition from the 3d state of Cu to the 2p state of N and 3p state of Mg in VB, respectively. The dielectric peak of Mg–N codoped CuAlO$_2$ can be attributed to the transition of electrons from 3d state of Cu to the state formed by the hybridization of 3p state of Mg and 2p state of N in VB. The above results are consistent with the results of band structures and density of states calculation. The width of the dielectric peak in the low energy direction of Mg–N codoped CuAlO$_2$ is wider than that of Mg-doped CuAlO$_2$ and close to that of N-doped CuAlO$_2$ indicating that the localization of the hybrid state formed by codoping of Mg and N become weak. Therefore, the method of Mg–N codoping is beneficial to the increases of hole concentration for Mg–N codoped CuAlO$_2$.

$$R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$

(6)

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}$$

(7)

Figure 6. Imaginary part $\varepsilon_2(\omega)$ of dielectric constant of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO$_2$.

Figure 7. Absorption $\alpha(\omega)$ spectra of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO$_2$. 

The width of the dielectric peak in the low energy direction of Mg–N codoped CuAlO$_2$ is wider than that of Mg-doped CuAlO$_2$ and close to that of N-doped CuAlO$_2$ indicating that the localization of the hybrid state formed by codoping of Mg and N become weak. Therefore, the method of Mg–N codoping is beneficial to the increases of hole concentration for Mg–N codoped CuAlO$_2$. 

Mater. Res. Express 8 (2021) 015904 W Liu et al
Figure 7 shows the absorption spectra of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂. The absorption edge located at about 3 eV can be attributed to the electron transition from VB to CB. The absorption edge of Mg-doped, Mg–N codoped and N-doped CuAlO₂ moves towards the lower energy due to the decreases of band gap for doping, which is consistent with the calculated results of band structure and density of state. For the doped CuAlO₂, a new absorption peak is observed in the area of lower energy. From the calculation of band structure, the acceptor level can be found located at about 0.72 eV, 0.19 eV and 0.24 eV above the EF for N-doped, Mg-doped, and Mg–N codoped CuAlO₂, respectively. Therefore, the optical absorption of N-doped and Mg-doped CuAlO₂ in lower energy can be attributed to the transition of electron from 3d state of Cu to 2p state of N and 3p state of Mg in VB, respectively. For Mg–N codoped CuAlO₂, the acceptor level is formed by the hybridization of 2p state of N and 3p state of Mg. Therefore, the optical absorption of Mg–N codoped CuAlO₂ in lower energy can be attributed to the electron transition from 3d state of Cu to the acceptor level formed by Mg–N codoping. The acceptor level of Mg-doped and Mg–N codoped CuAlO₂ is near the top of the VB, therefore, the absorption coefficient of Mg-doped and Mg–N codoped CuAlO₂ in the area of low energy is larger than that of undoped and N-doped CuAlO₂. Above results are consistent with the calculation results of band structures and density of states.

The reflectance spectra of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂ are shown in figure 8. In the area of low energy, the reflectivity of doped CuAlO₂ is larger than that of undoped CuAlO₂, especially for Mg-doped and Mg–N codoped CuAlO₂. Therefore, undoped CuAlO₂ is the best choice while CuAlO₂ is used as transparent electrode or hole transport layer in photovoltaic devices. Otherwise, it will affect
the absorption of visible light and reduce the photoelectric conversion efficiency of the photovoltaic devices. For Mg-doped and Mg–N codoped CuAlO₂, the reflectivity show decreases significantly with the increase of energy in the area of low energy. The energy loss function \( L(\omega) \) can be used to describe the energy loss of a fast electron traversing in material. Figure 9 shows the energy loss spectra of undoped, N-doped, Mg-doped, and Mg–N codoped CuAlO₂. For undoped CuAlO₂, there is no loss of energy in the area of low energy. However, for N-doped, Mg-doped, and Mg–N codoped CuAlO₂, the energy loss in the area of low energy is significantly increased. The energy loss of Mg-doped and Mg–N codoped CuAlO₂ is larger than that of undoped and N-doped CuAlO₂. The increase of energy loss after doping indicates that the inelastic scattering is enhanced. The energy loss peaks of Mg doped CuAlO₂ and Mg–N codoped CuAlO₂ are 1.029 eV and 1.126 eV, respectively. The peaks located at 1.029 eV and 1.126 eV correspond to the fast decreases of the reflectivity, which can be attributed to the transition of electron from the 3d state of Cu to the 3p state of Mg and the 2p states of N.

4. Conclusion

The band structure, density of states and optical properties of Mg-doped, N-doped and Mg–N codoped CuAlO₂ were investigated by using first-principles calculation based on density functional theory. Due to the difference of ionic radii between doping atoms and host atom, the changes of bond length and the expands of cell volume are found in N-doped, Mg–N codoped and Mg-doped CuAlO₂. The acceptor level induced by 2p state of N in N-doped CuAlO₂ is very deep. Although the 3p state of Mg form a shallower acceptor level, the Mg-doped CuAlO₂ has indirect band gap. Whether the deep acceptor level or the indirect band gap, it is unfavorable to p-type doping or light emission. For the hybridization of 3p state of Mg and 2p state of N, the Mg–N codoped CuAlO₂ not only has a direct band gap, but also has a shallower acceptor level (about 0.24 eV above the top of the valence band). Compared with undoped CuAlO₂, the optical parameters of dielectric constant, refractive index, absorption coefficient, reflectivity and energy loss function for N-doped, Mg–N codoped and Mg-doped CuAlO₂ show increases in the area of low energy, which can be attributed to the increases of the degree of the disorder of lattice structure for doping. Based on the above results, Mg–N codoping for CuAlO₂ is an effective way to improve its light emission properties and acceptor ionization rate, which will be beneficial to p-type doping and application of CuAlO₂ in optoelectronic devices.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 61504118) and the Natural Science Foundation of Jiangsu Province (No. BK20130423).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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