First-principles calculation of electronic structure of $Mg_xZn_{1-x}O$ codoped with aluminium and nitrogen*

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Aiming at developing p-type semiconductors and modulating the band gap for photoelectronic devices and band engineering, we present the *ab initio* numerical simulation of the effect of codoping ZnO with Al, N and Mg on the crystal lattice and electronic structure. The simulations are based on the Perdew–Burke–Ernzerhof generalised-gradient approximation in density functional theory. Results indicate that electrons close to the Fermi level transfer effectively when Al, Mg, and N replace Zn and O atoms, and the theoretical results were consistent with the experiments. The addition of Mg leads to the variation of crystal lattice, expanse of energy band, and change of band gap. These unusual properties are explained in terms of the computed electronic structure, and the results show promise for the development of next-generation photoconducting devices in optoelectronic information science and technology.

Keywords: first-principles, electronic structure, ZnO, doping

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1. Introduction

Zinc oxide (ZnO) is a direct, wide band-gap, II–VI compound semiconductor with an energy gap E_g of 3.37 eV[1] and its exciton-binding energy being up to 60 meV at room temperature. ZnO is particularly interesting because it exhibits a superior performance,[2,3] and it is used as a host in solar cells,[4] liquid crystal display,[5] UV semiconductor lasers,[6] and transparent conductive films.[7,8] Currently, a significant amount of research is being devoted to metal-doped ZnO film. Al-doped ZnO,[9,10] Ga-doped ZnO,[9,11] and In-doped ZnO[9,12] are reported to be all high-quality n-type transparent conductive films. In addition, p-type doped ZnO has received some attention, but this material is unstable and difficult to control.

Theoretical and experimental research has proven that N is the best element to prepare p-type doped II–VI semiconducting oxides.[13] However, experiments[14−19] have shown that intrinsic ZnO has many types of defects, making it difficult to fabricate N-doped ZnO. Over the past decade, reports have appeared of a new p-type transformation in ZnO.[20] In 1999, Yamamoto and Yoshida[21] proposed the 'donor-acceptor' codoping theory to explain the reduction in the Madelung energy upon n-type doping. If the Madelung energy is reduced, the p-type characteristics of the material will be maintained and the multi-element codoped material will be more stable and controlable. This 'donor-acceptor' method can thus raise the doping concentration of N and create shallow acceptor levels. Furthermore, (Al, 2N) codoping[22,23] can reduce the Madelung energy significantly. And Al is innocuous and environmentally friendly as compared to Ga, so the (Al, 2N) codoped thin films are expected to be the most promising p-type films substituting for the (Ga, 2N) codoped p-type films. The present study is based on adding Mg into (Al, 2N) codoped materials to obtain multi-element codoped ZnO with a continuously tunable band gap.

2. Computational method

Our simulations are based on density functional theory (DFT) and use the Cambridge Serial Total Energy Package (CASTEP) software.[24] The core region and valence electrons of the atoms in the supercell of intrinsic and doped ZnO are described within the generalised gradient approximation (GGA), employing the Perdew–Burke–Ernzerhof (PBE) functional form.[25] The valence-electron configuration chosen for O, Zn, Al, N, and Mg atoms is $2s^22p^4$, $3d^{10}4s^2$, $3s^23p^1$, $2s^22p^3$, and $2p^63s^2$, respectively. Numerical integration of the Brillouin zone is performed using a 4×4×2 Monkhorst–Pack[26,27] k-point sampling, and the cut-off energy of the plane wave is assumed to be 340 eV.

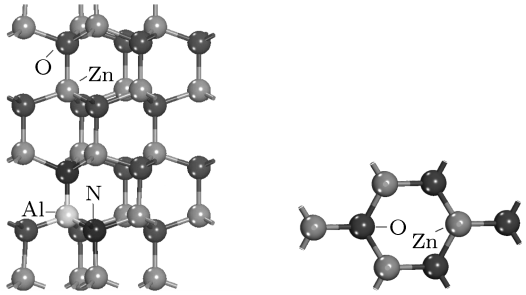
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The numerical calculations are performed by considering a 2×2×2 ZnO supercell that contains sixteen atoms of each element of Zn and O.

For atomic substitutions in the ZnO supercell (Fig. 1), we consider that Al atoms substitute for Zn ions and N atoms substitute for O atoms because they are the two nearest-neighbouring anion sites of an Al atom. This substitution produces the N–Al–N system, which is called the (Al, 2N) codoping pair.



(a) scenograph (b) planform

Fig. 1. Schematic of the 2×2×2 supercell.

The element Mg will replace the Zn ions. The lattice constants chosen for intrinsic wurtzite ZnO (i.e., before the lattice parameters are changed to those of the codoped lattice) are $a = 3.249$ Å (1 Å=0.1 nm) and $c = 5.205$ Å. In the optimisation process, the energy variation and the maximum tolerances of force, stress, and displacement are 10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa, and 0.001 Å, respectively.

3. Results and discussion

3.1. Calculation of ZnO film parameters

To obtain the lattice attributes of intrinsic ZnO and fix the lattice constants a, b, and c, we optimise the supercell and calculate the energy band, the density of states (DOS), and the partial DOS (PDOS). The results are shown in Fig. 2. The zero line is the Fermi level and the band gap is 0.735 eV, which is similar to the result of other DFT calculations (e.g., Schleife *et al.*[28] found a band gap of 0.73 eV and Janotti *et al.*[29] gave a value of 0.80 eV). The calculated band-gap energy is far less than the experimentally determined band-gap energy of 3.37 eV. Generally, the underestimation of the band-gap energy E_g is due to the choice of the exchange–correlation energy within the CASTEP simulation module.[30,31] In intrinsic ZnO, the calculated Zn-3d level is higher than the experimentally observed one, the Zn-3d and O-2p levels interact with each other, the width of valence-band increases, and the band gap decreases. However, this does not affect the analysis of the theoretical electronic structure of ZnO, especially for the band-gap structure of the G point that agrees with previous theoretical and experimental results.[32]

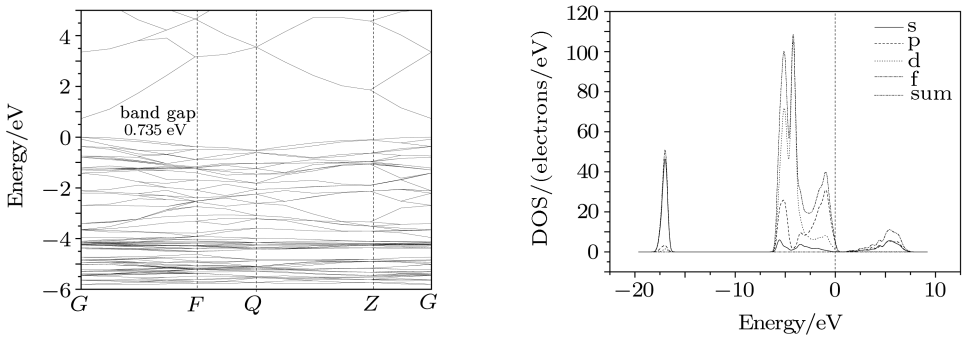


Fig. 2. Energy band diagram and the DOS.

Our calculation shows that the intrinsic ZnO is a typical direct-gap semiconductor with the most probable transition point being the G point. The ZnO valence band can be divided into two parts: the region of −4.0 to 0 eV originates from O-2p levels and that of −6.0 to −4.0 eV originates from Zn-3d levels, and the portion of the valence band near −18 eV originates from O-2s levels, while interactions with other portions of the valence band are weak. The conduction band originates from Zn 4s levels, and it causes the local DOSs to shift to lower energies. Results indicate that ZnO is a metal-oxide semiconductor with high ionicity and weak covalent bonds.

3.2. Calculation of lattice parameters for multi-element codoped ZnO

To obtain the lattice parameters of multi-element codoped ZnO, the (Al, 2N) codoping pair is built in the 2×2×2 ZnO supercell, then Mg is inserted into the supercell which is optimised to obtain the lattice parameters. We can modulate the Mg content to control the characteristics of the ZnO. The computation model is shown in Fig. 1. Variations of the lattice parameters α and β are approximately 0.500%, and that of γ is approximately 0.200%. It is clear that as α decreases, β increases. Furthermore, γ varies with increasing number of Mg atoms in the supercell, and the three angles of it all become increasingly stable as the Mg content increases. The cell volume also increases with increasing Mg content. As the Mg content changes from 0% to 93.75%, the lattice constants a and b increase from 6.557 to 6.708 Å, and c decreases from 10.64 to 10.38 Å. The cell volume increases by 2.310%. Thus, as the Mg content increases, a and b get longer whereas c gets shorter. The angles α, β, and γ vary over a small range. These subtle variations in unit-cell length, angles and lattice parameters will influence the material characteristics.

3.3. Calculation and analysis of electronic structure

Figure 3(a) shows that the DOS of the 2×2×2 supercell codoped with (Al, 2N) is similar to the intrinsic ZnO except for the small peak at −12.50 eV. These peaks come from N 2s and Al 3d levels, as shown in the PDOS of ZnO codoped with (Al, 2N) (see Fig. 2). It is noteworthy to find that the electronic structure of the valence band near the Fermi level varies when the supercell is doped with Al and N. In the supercell, the Fermi surface enters the valence band, and there are more electrons near the Fermi surface than in intrinsic ZnO. The band edge consists mainly of hybridised O-2p and N-2p levels and the valence-band maximum is determined by the N-2p level. From Fig. 3, it is clear that the N-2p level has induced an increase in the number of electrons near the Fermi surface. Furthermore, the Al $3s^2$ $3p^1$ peaks are all weak near the Fermi surface, so they are not helpful to p-type conduction. The band gap of the doped supercell is only 0.008 eV. The PDOS of N (see Fig. 3(b)) shows that the N-2p levels increase the valence-band maximum, but the bottom of the conduction band does not change, so the band gap is reduced. The p-type electrical conductivity of the material is enhanced, which is the aim of codoping with (Al, 2N). To reduce the band gap due to N, we introduce Mg into the material to modulate the band gap.

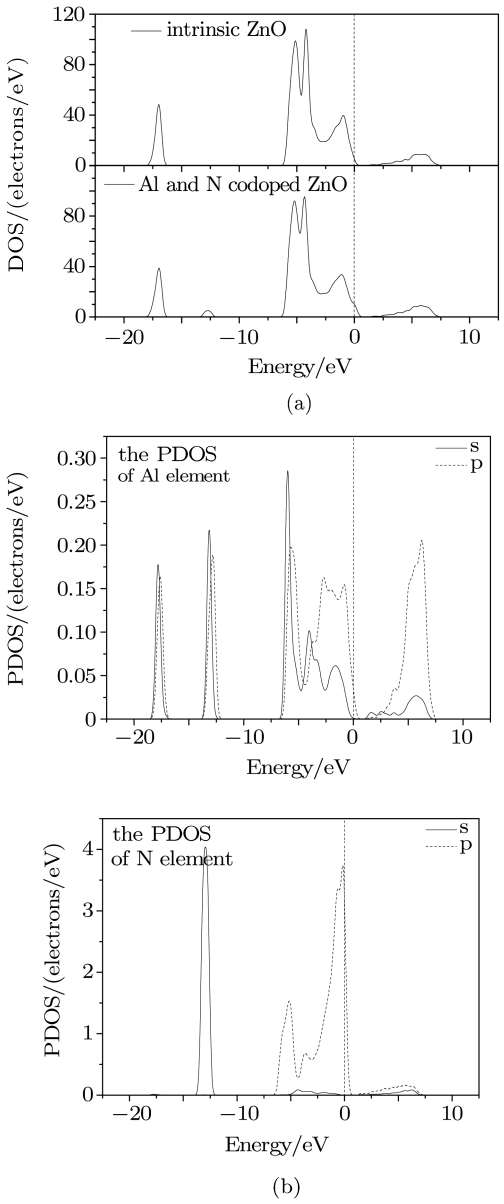


Fig. 3. (a) The DOS of the intrinsic ZnO and that of Al and N codoped ZnO; (b) the PDOS of Al and N in the (Al, 2N) codoped ZnO material.

When Mg is doped into the material (thereby the Mg content is raised), the ZnO material codoped with Al and N becomes a new multi-element codoped ZnO alloy semiconductor. Since the Mg content influences the electronic properties of the material, the variation in the electronic structure can be achieved by varying the Mg content or DOS. As explained above, the band gap calculated using DFT is significantly smaller

than the experimental value for the solid-state material. However, this is acceptable when the results are obtained for the same supercell and the same computing environment. In what follows, we will compare the band gap and the DOS as a function of Mg content.

Figure 4 shows the DOS of the ZnO supercell codoped with Al and N for different Mg contents. We find that the Fermi surface enters the valence band and the ZnO material codoped with Al and N exhibits good p-type conduction. When the supercell is doped with Mg, as shown in Fig. 4, a peak at approximately 10 electrons/eV occurs at −40 eV with a width of approximately 1.723 eV. The PDOS (Fig. 5) shows that the peak originates from Mg-2p levels. Because the DOS remains stable near the Fermi surface, the Al-, N-, and Mg-codoped material remains a good p-type conductor. Figure 5 shows that this p-type conduction is maintained when the supercell is doped with Mg.

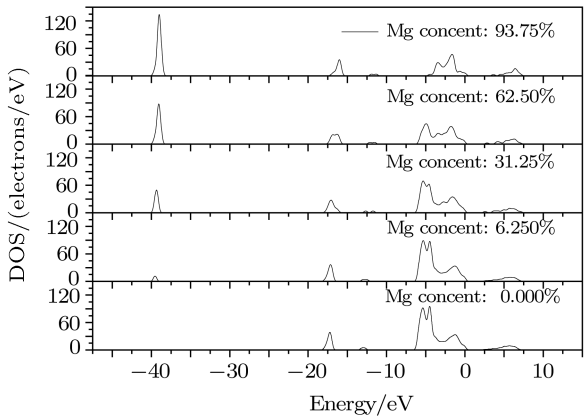


Fig. 4. The DOS of Al and N codoped ZnO supercell with different number of Mg atoms. The contents of Mg are 0, 6.250%, 31.25%, 62.50%, 93.75%, respectively.

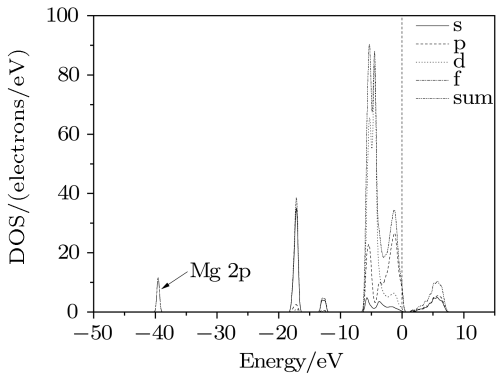


Fig. 5. The DOS of the (Al, 2N) codoped ZnO supercell with the Mg concent of 6.250%.

Figure 4 shows the variation of DOS with Mg contents in the 2×2×2 supercell. As shown in Fig. 5., when Mg is doped into the supercell, there is a peak, which is caused by Mg-2p, located at −40 eV. When the content of Mg increases, the peak rises because the number of Mg-2p electrons increases. And there appears another peak which comes from Zn-3d; the peak will reduce as the Mg content rises. When the number of Mg atoms increases in the supercell, the number of Zn-3d electrons will reduce relatively, and the peak will decline. Figure 4 shows another trend also: when the Mg increases, the peak, which is from the electrons near the valence band, becomes narrow (the peak width get narrow), the centre of the valence band moves toward Fermi surface, but the electrons located at the top of the valence band will shift to the low-power zone. And the conduction band which comes from Zn-4s shifts to the high-power zone,[33] so the distance between the valence band and Fermi surface increases and the band gap gets large. The ZnO alloy material will change from semiconductor to insulator.

Figure 6 shows that when the supercell is doped with N, the p-type characteristics of the system become stronger than in intrinsic ZnO; more electrons are present in the area of the Fermi surface and the Fermi level goes deeper into the valence band. From Figs. 6 and 7, we see that the highest concentration of electrons near the Fermi surface occurs for low Mg content (6.250%), so p-type conduction is maintained. When Mg content is increased, the Fermi surface penetrates deep into the valence band of the complex system that is codoped with Al, N, and Mg; and the number of electrons near the Fermi surface is reduced.

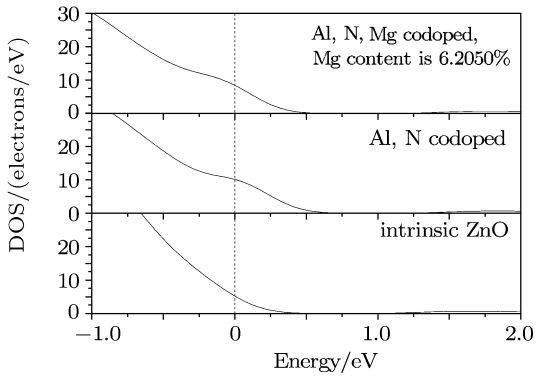


Fig. 6. The DOS of three kinds of ZnO material.

Thus the p-type conduction of the complex alloy, although maintained, is weakened. Chen and Shen[34] showed that the $Mg_xZn_{1-x}O$ alloy takes the rock-salt

structure when the Mg content exceeds 45%. Similar to what is reported in the literature, we find that Al, N, and Mg codoping can lead to high-quality p-type $Mg_xZn_{1-x}O$ film, and our calculation also shows that the multi-element alloy exhibits p-type conduction, which agrees with experimental results.

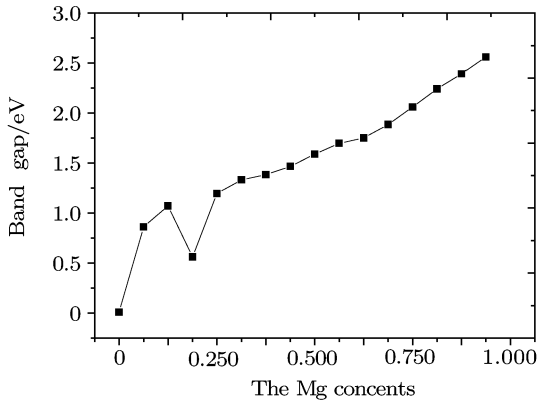


Fig. 7. The relation between the Mg contents and the band gap.

3.4. Variations of the band gap in multi-element codoped material

There are two important conditions that should be taken into account in designing modern ZnO-based photoelectric devices: to obtain the p-type semiconductor and to modulate the material band gap. When the ZnO based material is designed and manufactured, the ZnO multi-element alloy is often used to solve this to address the band-gap issue. To optimise the electronic and optical properties, we can change the band-gap structure and energy-band diagram. ZnO is a new type of broad-band-gap semiconductor material, and when it is doped with Mg, the band gap is modified. Thus, it becomes possible to optimise the electronic properties of this new ZnO material for the application in photoelectronic devices.

In Fig. 7, we see that the band gap of the multi-element codoped ZnO alloy increases with increasing Mg content, and that the relationship is quasi-linear. When the Mg content is in the range of 0 to 12.50%, the band-gap energy increases dramatically. However, when the Mg content is in the range of 12.50%–18.75%, the band-gap energy reduces obviously. When the Mg content exceeds 18.75%, the band gap increases again and the result is as we expected. And the variation of band-gap energy becomes approximately linear with Mg content in Fig. 8.

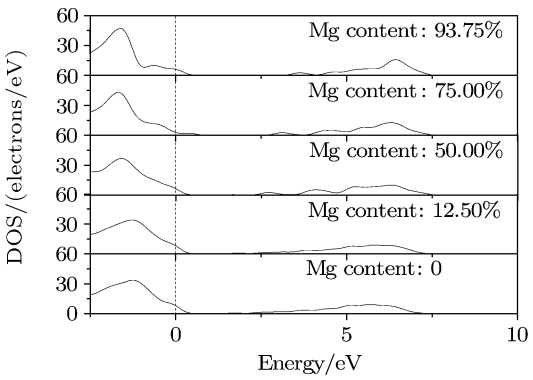


Fig. 8. The DOS of the complex alloy in which the Mg content is different.

The Mg atom that is inserted into the supercell influences the lattice parameter and electronic structure. As shown in Fig. 8, the conduction band (originateing from the Zn-4s level) and the DOS peak position shift to the high-energy zone. Figures 6 and 8 show that, under the same conditions, the valence-band maximum is determined by the N-2p and O-2p levels, which are almost constant upon doping with Mg. However, the number of electrons near the Fermi surface is reduced. The position of the valence-band peak, which is near the Fermi surface, shifts to the low-energy zone and the peak width narrows, so the electrons near the valence-band maximum shift to the low-energy zone and are reduced in number, the distance between the valence-band maximum and the bottom of the conduction band becomes larger, and the interaction between electrons weakens. Electronic transitions thus become difficult and the band gap becomes larger for higher Mg content.

This calculation shows that the relationship between the band gap energy and the Mg content is not strictly linear, and that rapid transitions appear at specific Mg contents. In particular, at the two inflexion points, the band gap varies strongly with Mg content. A large discrepancy still exists between the theoretical and experimental results, but when we adopt the same conditions for both, the calculations appear correct and reliable. The previous experiment shows that doping ZnO with Mg is an effective method to control the band gap. Our calculation indicates that this new multi-element codoped ZnO material also maintains its p-type characteristics.

4. Conclusions

In summary, we have computed the electronic structure and band gap of ZnO doped with Al, N,

and Mg based on the PBE GGA of DFT. Calculations show that the lattice parameters a, b, c, the cell volume, and the band-gap energy all vary when a ZnO supercell is codoped with Al, N, and Mg. The cell parameters a and b and the band gap all increase with increasing Mg content, but the cell parameter c is reduced. The supercell codoped with Al and N exhibits p-type conduction, which is maintained upon doping with Mg. The band gap becomes larger with increasing Mg content, because of the narrowed width of the DOS-peak close to the Fermi surface, the electron energy distribution and valence-band maximum shifting to a lower energy, and the bottom of the conduction band shifting to higher energy.

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