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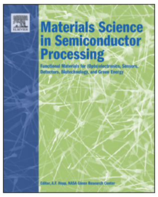

First-principles study of p-type nitrogen/aluminum co-doped zinc oxide

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ABSTRACT

First-principles calculations have been performed to investigate the electronic structures and the defects formation energies of the pure and nitrogen/aluminum (N-A1) co-doped zinc oxide. The calculated results of the pure ZnO using LDA+U method show band gap and lattice parameters are in reasonable agreement with previous data. Incorporation of N into ZnO host induces distortions of the lattice. According to the results, the Fermi-level of Al doped ZnO shift upward into conduction band and show n-type conductivity, while codoped structures show p-type conductivity. The defects formation energies of Al doped structure on Zn-rich and O-rich conditions are low. When codoped with N, the complexes exhibit high defects formation energy on O-rich condition, indicating it is difficult to realize p-type ZnO in this case. On Zn-rich condition, the codoped structures display lower defects formation energies and show p-type conductivity. From hole carriers analysis, it is shown that the carriers in N-Al doped ZnO possess a better transfer character. All these results indicate that codoped ZnO structures are beneficial for the realization of p-type ZnO.

1. Introduction

Zinc oxide (Zno) is a promising material for short wavelength optoelectronic devices applications, such as ultraviolet (UV) lasers, light-emitting diodes and solar cells [1,2]. ZnO has a wide direct band gap of 3.37 eV and its lattice constants are similar to GaN, which is extensively used in optoelectronic applications [3]. The exciton binding energy of ZnO is 60 meV at room temperature, larger than 25 meV of gallium nitride (GaN), and it is expected to be much brighter than GaN based light emitters [4]. Achieving an ideal p-type material is fundamental to manufacture optoelectronic devices with p–n junctions. However, it is difficult for ZnO to dope nitrogen and get p-type conductivity similar to most oxide materials [5]. This is mainly because the electronegativity of oxygen is larger than N, and ZnO has a lower valence band maximum (VBM) than GaN. Therefore, acceptor levels are deep in ZnO. The p-type doping problem of ZnO has restrained the full utilization of this material as a novel optoelectronic material so far and has become a research hotspot [6–9].

Currently, most investigations of the p-type ZnO are focused on the dual doping technologies. Theoretically, group-I elements substitute for Zn sites in ZnO lattice can act as shallow acceptors, but these dopants tend to occupy the interstitial sites, this is because of the electronegativity difference between Zn and group-I elements and the relatively small atomic radius. The covalent radius and electronegativity of O are 0.63 Å and 3.44, respectively. For the group-V elements, it is regarded that N is the most suitable dopant for its covalent radius and electronegativity (0.71 Å and 3.04, respectively) are approximate to O, thus N should

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be apt to substitute O atom and act as acceptor. However, it is still difficult to achieve ideal p-type conductivity in N-doped ZnO due to low dopant solubility as well as high defect ionization energy. Yamamoto et al. [10] found that n-type doping can lower the Madelung energy of ZnO while p-type doping does the opposite, resulting in instability of the lattice. Therefore, the acceptor–donor co-doping method could be a reasonable approach to improve and control conductivity, for it will decrease the Madelung energy and enhance the incorporation of acceptor and stable p-type ZnO can be obtained. In the aspect of the experiments, Zhu et al. [11] prepared N–Al codoped ZnO thin films using high-temperature homo-buffer layer and the films showed p-type conductivity. Wang et al. [12] studied the chemical bonding states of N, Ga single and codoped ZnO films. It is found that the flux ratio of N/Ga had a significant influence on the bonding states of dopants. In first-principles calculations, Guo et al. [13] investigated (Sb, N) doped ZnO, the results showed that Sb_{Zn}–4NO structure had lower defects formation energy and smaller hole effective mass. Wang et al. [14] studied Ag-based p-type ZnO, the calculated conclusions showed that Ag doped structure was beneficial to the realization of p-type ZnO. Xie et al. [15] calculated the electrical properties of N, Ga codoped ZnO, and the results showed that 2N–Ga codoping can obtain a high quality and stable p-type ZnO.

In this work, we present theoretical studies on the properties of N, Al codoped ZnO, including their geometric/electronic structures and defects formation energies. Based on these results, the feasibility of N and Al codoped p-type ZnO will be discussed.

2. Model and methods

First-principles density functional theory (DFT) based on the local density approximation (LDA) suffers from the well known gap underestimate problem. This is particularly true for the calculation of highly correlated systems which exhibit strong effective Coulomb interactions between localized electrons. One of methods to correct this problem is LDA+U [16,17]. The Hubbard parameter is an on-site Coulomb repulsion parameter incorporating part of the electron correlation absent in LDA. This calculation is based on DFT and the LDA+U method is used to correct this underestimate [18]. The theoretical calculations are performed using first principles approach based on LDA+U for exchange-correlation potential within the framework of DFT. The pseudopotentials involve 12, 6, 5 and 3 valence electrons for Zn ($3d^{10}4s^2$), O ($2s^22p^4$), N ($2s^22p^3$) and ($3s^23p^1$), respectively. In this work all dopants are doped into ZnO in the form of substitutions. The calculations were performed by employing a plane-wave basis set implemented in the CASTEP. A $5\times5\times2$ k-point mesh and a 380 eV cutoff energy for the plan-wave expansion are used for the calculations. All the ions are allowed to relax until the force acting on each ion is less than 0.01 eV/Å, and the internal stress upon each atom is less than 0.05 GPa. The U values are: $U_{d,Zn}=10.5$ eV, $U_{s,Zn}=0$, and $U_{p,O}=7.0$ eV.

3. Results and discussion

3.1. Geometric structure

We begin calculations with the experimental lattice parameters to create the unit cell and optimize the bulk structure of wurtzite ZnO. The calculated results in Table 1 show that ZnO lattice constants are slightly overestimated when employed a typical feature of LDA+U methods. But the overestimated is less than 3%, which is in good agreement with the experimental values [19]. The calculated lattice parameters of doped ZnO mainly depend on the kinds of dopants as well as the quantity of the dopants. Compared with pure ZnO, the value of c/a of N doped structures increases. Since the covalent radius of N is greater than that of O, the lattice parameters become larger as N is on the O site. When Al is on the Zn site, the lattice parameters of ZnO are expanded obviously which attributes to Al^{3+} repulsion the surrounding ions.

3.2. Electronic structure

Fig. 1(a) shows the calculated band structures of pure ZnO. The Fermi-level is specified to zero in this paper. In the graph, the conduction band minimum (CBM) and the VBM are at the same k-point (G), indicating a direct gap semiconductor. The calculated band gap is 2.77 eV, which is less than the experimental data of 3.37 eV. This is a common underestimate of the LDA or GGA [22], but this LDA+U result is closer to the experimental data [23]. The lower valence band of pure ZnO around 10 eV is mainly originated from Zn 3d states and this section changes slowly, due to which the 3d states of Zn are filled with electrons. The gentle change of the upper valence band from the O 2p compared with the bottom of conduction band from Zn 4s illustrate that larger hole carriers effective mass and a smaller mobility. The VBM and the CBM are mainly dominated by O 2p and Zn 4s states, respectively, which is also proved by experimental results [24,25].

Fig. 1(b) shows the TDOS of ZnO and the PDOS of O and Zn atoms, and the Fermi-level was set to zero as usual. It can be seen that the valence band is divided into three regions: the lower part from −17 to −15 eV, the middle

Table 1
Calculated structural parameters of pure and doped ZnO structures compared with experimental and Ref. values.

System	ZnO	N–ZnO	Al–ZnO	(N,Al)–ZnO	(2N–Al)–ZnO	(3N–Al)–ZnO	Expt. [19]	Ref. [20,21]
a/nm	3.271	3.273	3.282	3.277	3.286	3.279	3.249	3.289
c/a	1.611	1.618	1.635	1.621	1.633	1.631	1.602	1.614