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First-principle investigation of K–N dual-acceptor codoping for *p*-ZnO

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ABSTRACT

A novel dual-acceptor strategy was proposed for obtaining *p* type ZnO by codoping nitrogen (N) with potassium (K). Based on density functional theory within the local density approximation, a first-principle investigation has been performed on the electronic structure and main defects of K–N codoped wurtzite ZnO crystal. After doping K and N simultaneously, an acceptor shallow level appeared above valence band maximum approximate 0.24 eV, which was lower than that of monodoping K or N. It indicated that K–N dual acceptor codoping will be a benefit for obtaining more stable *p* type conductivity ZnO than mono-doping does. Additionally, such point defects as Zn vacancy in (K–N): ZnO system acted as a deep acceptor (0.41 eV) and was not a main source for hole carriers; H interstitial, however, behaved as an unfavorable donor to compensate acceptor level.

1. Introduction

The *p* type doping of zinc oxide (ZnO) is an intractable issue mainly due to its higher acceptor formation energy and ionization energy, resulting in the limited acceptor impurity solubility and charge hole carriers density [1,2]. Although nitrogen (N) element was once considered as an ideal dopant among VA group [3–5] owing to its lowest *p* orbit level, mono-doping N had not achieved expected results because of its still higher defect formation energy (No: 0.35 eV above valence band maximum-VBM) [6–8]. Group IA elements, especially Li/Na, possess a relatively shallow substitutional level (Li_{Zn}: 0.09 eV; Na_{Zn}: 0.17 eV) [3]. Unfortunately, Li/Na with smaller ionic radius has a strong tendency to form interstitial rather than substitutional defects, while the interstitials usually behave as an undesired donor. Recent years codoping strategies, such as donor-acceptor or dual-acceptor, have been proposed for lowering acceptor transition level [9–13]. Among these, dual-acceptor Li/Na–N or Ag–N provided some inspiring results. It was speculated by the first principles calculations that M_{Zn}–N_O (M refers to Li/Na or Ag) complex might be a main source of shallow acceptor level and made contribution to *p* type conductivity [14–16]. Nevertheless, Duan et al. argued that the acceptor was still Li_{Zn} other than Li_{Zn}–N_O even in (Li–N):ZnO system [11]. Additionally, Li/Na interstitials are also difficult to be completely depressed. An attempt for avoiding the problem is to codope larger radius acceptor such as Ag element with N. Theoretical prediction indicates that Ag–2N complex has a low transition level at about 0.20 eV [17,18]. However, Ag and N tend to form nearest-neighboring pairs and triangles, which will increase acceptor energies and thus lower the doping efficiency [19].

In this paper, we proposed a novel dual-acceptor route for *p*-ZnO by codoping N with another IA member, potassium (K) element. Based on the first-principles

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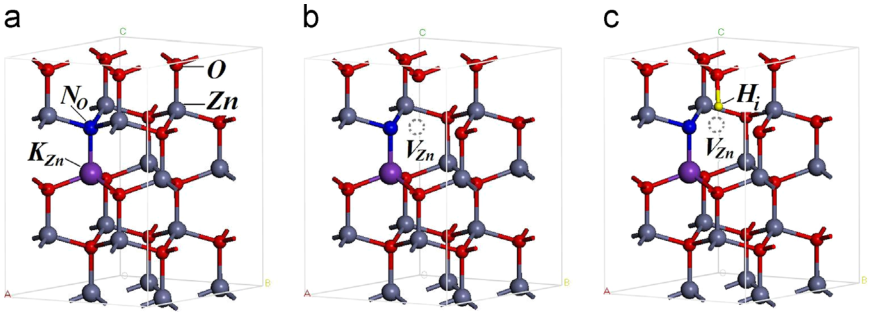

Fig. 1. Crystal structure of wurtzite ZnO 2 × 2 × 2 supercells with point defects: (a) nitrogen substituting for oxygen atom (N_O) and potassium for zinc atom (K_{Zn}) in codoped ZnO; (b) zinc vacancy (V_{Zn}) nearest to the N_O substituting sites; (c) hydrogen interstitial (H_i) nearest to the zinc vacancy.

calculations, the electronic structure of (K–N):ZnO without and with intrinsic defects (Zn vacancy and H interstitial) was investigated. Meanwhile, the substitutional defect levels were also calculated for interpreting the higher solubility of K and N, which may pave a new way to prepare ZnO with stable *p* type conductivity and high hole carriers density.

2. Theoretical model and computational method

The crystal structure of perfect ZnO model is a hexagonal wurtzite, belonging to the space group *P*63*mc* and *C*6*v*-4 symmetries. Its lattice constants are $a=b=0.325$ nm, $c=0.521$ nm, $c/a=1.60$, $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$. Each primitive cell is characterized by two interconnecting hexagonal close-packed (*hcp*) sublattices of Zn^{2+} and O^{2-}; each Zn^{2+} is surrounded by a tetrahedral O^{2-}, and vice-versa [20]. In a 2 × 2 × 2 supercell including 32 atoms, one substitutional K atom for Zn (K_{Zn}) and one N atom for O (N_O) have been doped. The defects of Zn vacancy (V_{Zn}) and H interstitial (H_i) are also constructed near to the doping sites, as shown in Fig. 1.

All calculations were carried out by the first principles approach based on local density approximation (LDA) for exchange-correlation potential within the framework of density functional theory (DFT). The pseudopotentials involving 12, 6, 9, and 5 valence electrons for Zn ($3d^{10}4s^2$), O ($2s^22p^4$), K ($3s^23p^64s^1$) and N ($2s^22p^3$), respectively, were performed by employing a plane-wave basis set implemented in Cambridge serial total energy package (CASTEP) code [21]. A 4 × 4 × 2 *k*-point mesh was employed for the Brillouin zone with a cutoff energy of 340 eV and convergence energy of 2×10^{-6} eV. The maximum Hellmann–Feynman forces and internal stress upon each atom were less than 0.05 V/Å and 0.1 GPa, respectively.

3. Results and discussion

3.1. Electronic structure of perfect ZnO

The band structure and density of state (DOS) of perfect wurtzite ZnO are shown as Fig. 2a and b, respectively. Typically, the valence band consists of two separated regions: the deeper region of −18.1 to −17.0 eV derived almost solely from O 2*s* bands; and the shallower region of −6.4 to0 eV, which can be further divided into the lower valence band of −6.4 to −3.7 eV and the upper valence band of −3.7 to ~0 eV. Obviously, in the lower band, Zn 3*d* electrons provide more attributions than O 2*p*; on the contrary, in the upper band, O 2*p* electrons are more predominant than Zn 3*d*. The conduction band between 0–8.8 eV is mainly occupied by O 2*p* and Zn 4*s* states. The highest valence band and the lowest conduction band are located at the same Γ-point, indicating wurtzite ZnO a typical direct band semiconductor.

The calculated band gap based on DFT is approximately 0.77 eV, which is underestimated when compared with experimental measurement gap of 3.4 eV [22]. As we see, Zn 3*d* bands have too high energy levels and are close to VBM, which makes them so active to overestimate the hybridization with O 2*p* bands and push valence band up. The overestimation about effect of Zn 3*d* ultimately leads to the reduction of band gap, at just about 20–30% of experimental value [10,11,13,15,23,24]. In order to match well the experimental gap, Hubbard *U* is often used for correcting the hybridization of 3*d*–2*p* [25]. Based on LDA+*U* approach, the location of 3*d* states is adjusted and depressed. Here, $U_{Zn}=2.5$ eV is determined with previous experience [26,27] as a corrected parameter for Zn 3*d* valence orbit. After that, the conduction band was shifted up, and the total band gap was improved to 3.2 eV (Fig. 2c), very close to the experimental value.

3.2. K–N dual-acceptor codoping ZnO

Fig. 3a–d respectively shows the partial DOS of un-, K-, N–and K–N co- doped ZnO (the energy range from −5 to 5 eV is only depicted, because more attentions are often paid on the electrons distributions nearby Fermi level). And Fig. 3e–f shows the PDOS of K and N valence electrons, respectively. As can be seen, the upper band of K:ZnO (Fig. 3b) extends obviously wider and the localization is not more severe than that of undoped ZnO (Fig. 3a). More electrons appear in VBM and move toward high energy zone, which is the co-contribution combining with K 3*p* and 4*s* electrons (from Fig. 3e). These electrons are easy to be activated at this level and form an acceptor, which is favorable for the conduction conversion from *n* to *p* type. In fact, we have experimentally prepared stable *p* type ZnO thin films by monodoping K [28] and theoretically identified the feasibility of