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Pushing p-type conductivity in ZnO by (Zr, N) codoping: A first-principles study

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ABSTRACT

Zr mono-doped and (Zr, N) co-doped ZnO are investigated by the first-principles calculations. It is found that Zr prefers to substitute Zn site under most growth conditions. The passive (N–Zr–N) complexes create a fully occupied impurity band above the valence-band maximum (VBM) of ZnO, which helps p-type conductivity by reducing the ionization energy, consistent with a new approach to overcome the doping asymmetry [Y.F. Yan, J.B. Li, S.H. Wei, and M.M. Al-Jassim, Phys. Rev. Lett. 98 (2007) 135506]. In comparison with (Ga, N) co-doping, (Zr, N) is found to be probably better dopants to push p-type conductivity in ZnO through the new approach with easier formation of the passive impurity band.

1. Introduction

The quest for a stable and reproducible p-type ZnO has been stimulated persistently by its great potential in many novel optoelectronic applications, such as transparent conducting contacts, blue lasers, and light emitting diodes [1,2]. In the past decades, most of the investigations were focused on the mono acceptor doping technology (such as Li [3], N [4], P [5], As [6], Sb [7] and the donor-acceptor pair co-doping method (such as Ga–N [8], Al–N [9], In–N [10]). Recently, it was reported that remarkably improved p-type conductivity ZnO films had been prepared by using zirconium and nitrogen (Zr–N) co-doping [11]. The reported p-type electrical resistivity of 0.026 Ω cm, Hall mobility of 4.4 $\text{cm}^2\ \text{v}^{-1}\ \text{s}^{-1}$, and carrier concentration of $5.5 \times 10^{19}\ \text{cm}^{-3}$ are significantly improved in comparison with other attempts [8–10]. In sharp contrast to the experimental attempts [8–10,12] on Zr involving doping for p-type ZnO, there has been no report on related theoretical studies. On the other hand, the co-doping concept has received extensive attention especially in wideband gap semiconductors, such as diamond and ZnO [13]. However, further systematic studies found that co-doping generally does lower its formation energy but not reduce the defect transition energy levels [14]. Very recently, a possible new approach to overcome the doping asymmetry was proposed based on the reduction of the ionization energies of dopants through introducing a mutually passivated impurity band [15].

In this work, Zr mono-doping and (Zr, N) co-doping in ZnO are studied by first-principles calculations, and it is found that: (i) The formation energy of a Zr substituting defect at a Zn site is much lower than that of interstitial Zr defect under most growth conditions. (ii) Passive (N–Zr–N) complexes create a fully occupied impurity band above the valence-band maximum (VBM) of the pure ZnO, suggesting that the p-type conductivity in (Zr, N) co-doped Zn could be explained by the effective doping of a mutually passivated impurity band proposed by Yan et al. [15]. The ionization energy of $\text{Ga}_{\text{Zn}}\text{–2N}_{\text{O}}$ and $\text{Zr}_{\text{Zn}}\text{–3N}_{\text{O}}$ acceptors may be reduced dramatically due to the impurity band. (iii) The relatively easier formation of the $\text{Zr}_{\text{Zn}}\text{–3N}_{\text{O}}$ complex suggests that (Zr–N) could be better dopants for p-type ZnO.

2. Model and methodology

All the calculations in this work are carried out by the first-principles plane wave method as implemented in the VASP codes [16], with the general gradient approximation [17]. The interactions between valence electrons and ions were represented with the projector augmented wave (PAW) pseudo-potentials [18]. The energy cutoff for the plane wave expansion is chosen at 500 eV. All the atoms are fully relaxed during the calculation until the Hellmann–Feynman forces have converged to 10 meV/Å. The calculated crystal lattice constants of ZnO ($a = 0.328$ nm, $c = 0.529$ nm) are used throughout the calculation, which are in

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excellent agreement with the experimental values ($a = 0.325$ nm, $c = 0.521$ nm). A 72-atom supercell is adopted for our modeling of Zr doped and (Zr, N) co-doped ZnO. A gamma centered $3 \times 3 \times 2$ k-point mesh is employed for the Brillouin zone integration of the 72-atom supercell.

The conductivity of a doped semiconductor is dominated by the concentration of defects which in principle depends on their formation energies. The formation energy (E^f) for a defect comprising atom D at charge state q under the equilibrium grown condition can be computed as [19,20]

$$E^f(D, q) = [E_{\text{tot}}(D, q) - E_{\text{tot}}^{\text{bulk}}(\text{ZnO})] + \sum_i n_i \mu_i + q(E_F + E_{\text{VBM}}). \quad (1)$$

Since the defect formation energies are conventionally defined with respect to the chemical potential of the elemental bulk(s), we express μ_i as $\mu_i = \Delta\mu_i + \mu_i(\text{bulk})$. Thus Eq. (1) could be rewritten as follows, exemplified with a Zr_{Zn} defect:

$$E^f(\text{Zr}_{\text{Zn}}, q) = \Delta E(\text{Zr}_{\text{Zn}}, q) + \Delta\mu_{\text{Zn}} - \Delta\mu_{\text{Zr}} + qE_F \quad (2)$$

$$\Delta E(\text{Zr}_{\text{Zn}}, q) = E_{\text{tot}}(\text{Zr}_{\text{Zn}}, q) - E_{\text{tot}}^{\text{bulk}}(\text{ZnO}) - \mu_{Zr}^{\text{bulk}} + \mu_{\text{Zn}}^{\text{bulk}} + q\varepsilon_{\text{VBM}}. \quad (3)$$

The atomic chemical potential should be less than that of the corresponding elemental bulk to avoid precipitation of the latter. That is,

$$\Delta\mu_i \leq 0. \quad (4)$$

Meanwhile, to maintain a stable compound ZnO and to avoid possible competing binaries, the chemical potentials must satisfy the following conditions:

$$\begin{aligned}
&\Delta\mu_{\text{Zn}} + \Delta\mu_{\text{O}} = \Delta H_f^{\text{ZnO}} \\
&\Delta\mu_{\text{Zr}} + \Delta\mu_{\text{O}} < \Delta H_f^{\text{ZrO}} \\
&\Delta\mu_{\text{Zr}} + 2\Delta\mu_{\text{O}} < \Delta H_f^{\text{ZrO}_2} \\
&3\Delta\mu_{\text{Zr}} + 4\Delta\mu_{\text{N}} < \Delta H_f^{\text{Zr}_3\text{N}_4} \qquad (5) \\
&\Delta\mu_{\text{Zr}} + \Delta\mu_{\text{N}} < \Delta H_f^{\text{ZrN}} \\
&2\Delta\mu_{\text{Ga}} + 3\Delta\mu_{\text{O}} < \Delta H_f^{\text{Ga}_2\text{O}_3} \\
&\Delta\mu_{\text{Ga}} + \Delta\mu_{\text{N}} < \Delta H_f^{\text{GaN}}.
\end{aligned}$$

Here ΔH_f^{ZnO}, ΔH_f^{ZrO}, $\Delta H_f^{\text{ZrO}_2}$, $\Delta H_f^{\text{Zr}_3\text{N}_4}$, ΔH_f^{ZrN}, $\Delta H_f^{\text{Ga}_2\text{O}_3}$, ΔH_f^{GaN} represent the formation enthalpies of ZnO and corresponding possible competing compounds. The calculated cohesive energy or formation enthalpy of the corresponding competing element bulks and compounds in (Zr, N) or (Ga, N) codoped ZnO are listed in Table 1. The calculated formation enthalpies are in good agreement with available experiment data (the errors are relatively large for O_2 and N_2 due to their open structures).

For the co-doped ZnO, the ionization energy of (Zr_{Zn}–3N_{O}) or (Ga_{Zn}–2N_{O}) acceptor with respect to the VBM is calculated by [21]

$$\varepsilon(0/q) = [\varepsilon_D^{\Gamma}(0) - \varepsilon_{\text{VBM}}^{\Gamma}(\text{host})] + [E(\alpha, q) - (E(\alpha, 0) - q\varepsilon_D^{k}(0))]/(-q), \quad (6)$$

where $E(\alpha, q)$, $E(\alpha, 0)$ are the total energies of the supercell at charge state q or neutral for defect α; $\varepsilon_D^k(0)$ and $\varepsilon_D^{\Gamma}(0)$ are the defect levels at the special k-points (averaged by weights) and at Γ-point, respectively; q is the defect charge state; and $\varepsilon_{\text{VBM}}^{\Gamma}(\text{host})$ is the VBM energy of the host supercell at Γ-point. Eq. (6) is to improve the VBM due to the limited supercell size effect for better comparison with experiments.

Regarding the impact of band gap error on the defect formation energies and corresponding transition levels (in particular, the donor levels), we have checked the charge density of the highest occupied state for the "neutral Zr_{Zn}" defect system, which is found to be similar to that of CBM state of a pure ZnO. This indicates that the Zr_{Zn} defect in a neutral system is actually a positively charged defect with electrons distributed in conduction bands. Therefore, the donor levels, especially those outside the LDA band gap, should be corrected for LDA band gap error. Here, we assume that the eigenvalues for conduction band states are shifted accordingly as the LDA band gap is corrected to the experimental value. Thus the transition levels outside the LDA band gap would shift up along with the conduction bands.

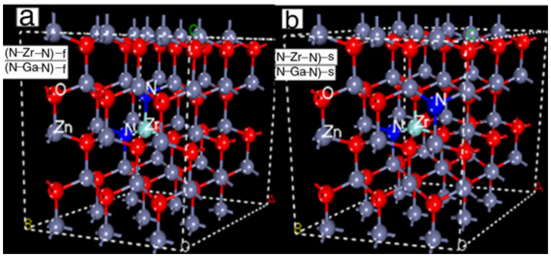

Fig. 2. (Color online) Crystal structures of ZnO supercells with codoping of Zr_{Zn} and two N_{O} (a) (N–Zr–N)-f configuration, and (b) (N–Zr–N)-s configuration. The corresponding Ga_{Zn}–2N_{O} configurations could be illustrated by replacing Zr with Ga.

3. Results and discussion

Fig. 1 shows the formation energies of the possible Zr mono doped defects, Zr_{Zn}, Zr_i and Zr_{O}, under O-rich ($\Delta\mu_{\text{O}} = 0$, $\Delta\mu_{\text{Zn}} = -3.54$ eV, $\Delta\mu_{\text{Zr}} = -11.40$ eV) or Zn-rich conditions ($\Delta\mu_{\text{O}} = -3.54$ eV, $\Delta\mu_{\text{Zn}} = 0$ eV, $\Delta\mu_{\text{Zr}} = -4.32$ eV). The maximum chemical potential of Zr is adopted here with the restriction from competing Zr–O compounds in Eq. (5), which corresponds to the Zr rich condition. Under an O-rich condition, the formation energy of Zr_{Zn} is much lower than that of the defect Zr_i or Zr_{O}, It indicates that Zr prefers the Zn site and Zr_i, Zr_{O} defects are difficult to form in Zr doped ZnO. Under a Zn-rich condition, the formation energy of Zr_{Zn} is still the lowest except in the $E_F < 0.2$ eV region, where Zr_i is the most stable defect. The Zr_{Zn} is found to be always in the +2 charge state after a simple LDA band gap correction to the transition levels as mentioned in Section 2.

Among the group-III and V co-doped ZnO, it was reported that the best p-type conductivity is achieved with Ga and N co-doping [8,22]. It was proposed that the formation of passive stoichiometric (Ga–N) complexes creating a fully occupied impurity band above the VBM of ZnO is crucial to the successful p-type doping in ZnO [15], which will significantly decrease the acceptor levels with electrons transiting from the top of the impurity band rather than the original VBM.

Two configurations of (N–Zr–N) complex are considered in ZnO as shown in Fig. 2(a) and (b). The configuration (N–Zr–N)-f is constructed with both N ions substituting two of the four first nearest-neighbor O sites of Zr_{Zn} (see Fig. 2(a)). The configuration (N–Zr–N)-s is constructed with one N substituting the first nearest-neighbor O site of Zr_{Zn}, and the other N substituting the second nearest-neighbor O site (see Fig. 2(b)). The optimal energy of configuration (N–Zr–N)-f is lower than that of (N–Zr–N)-s by 0.31 eV, which indicates N–Zr–N passive clusters could be formed in ZnO.

The calculated total DOS for the pure ZnO host, (N–Zr–N) complex doped ZnO, and (Ga–N) complex doped ZnO, are shown in Fig. 3. It reveals clearly that the formation of (N–Zr–N) complexes does not change the basic electronic structure, but generates an additional fully occupied impurity band above the VBM, consistent with the case of (Ga–N) co-doped ZnO [15]. Thus, the new