

X.-Y. DUAN
R.-H. YAO[✉]
Y.-J. ZHAO

The mechanism of Li, N dual-acceptor co-doped p-type ZnO

School of Physics, South China University of Technology, Guangzhou 514640, P.R. China

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ABSTRACT The formation of single defects and defect complexes are investigated in Li, N co-doped ZnO by the first-principles plane wave method with projector augmented wave (PAW) pseudo-potential technology. We find that: (i) p-type conductivity could be achieved in single Li doped ZnO under an O-rich condition, since the formation energy of Li_{Zn} acceptor is much lower than the interstitial Li_i ; (ii) the dual-acceptor complex $\text{Li}_{\text{Zn}}\text{-N}_{\text{O}}$ is unlikely to form, and the good p-type conductivity is mainly attributed to the Li_{Zn} acceptor, even in Li, N co-doped ZnO; (iii) the additional introduction of N may help compensate the single Li_i donor defects under certain growth conditions, but its role in the p-type conductivity in ZnO remains to be clarified.

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1 Introduction

ZnO is a novel semiconductor material and has many potential applications in next-generation short-wavelength optoelectronic devices, since it has a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV) [1]. However, a stable and reproducible p-type ZnO with good conductivity is difficult to fabricate, which is a bottleneck for practical ZnO-based applications. So far, most of the investigations have focused on the single acceptor doping technology, such as Li, N, P, As, Sb, and the donor–acceptor pair, such as Ga–N, Al–N, In–N, co-doped methods. Theoretically, Li and N are the best candidates for producing p-type ZnO considering the strain effects and energy levels of substitutional Li_{Zn} and N_{O} acceptors. Unfortunately, compensating donor defects accompanying these dopants, such as Li interstitials (Li_i) for Li doped ZnO and $\text{N}_2\text{-on-O}$ substitutions [$(\text{N}_2)_{\text{O}}$] in N doped ZnO, are often observed. Recently Li, N dual acceptor co-doped p-type ZnO were obtained by several research groups [2–5]. It was reported in [2, 3], that p-type conductivity of ZnO:(Li,N) films is evidently improved. The stability and conductivity of the ZnO sample are both better than individual Li or N doped ZnO. It was suggested in [4, 5], that the p-type conduction of the ZnO:(Li, N) could be resulting

from the formation of $\text{Li}_{\text{Zn}}\text{-N}$ complex acceptors, while [3], proposed that the dual acceptor co-doping could probably reduce the formation of the compensating defects, such as Li_i or $(\text{N}_2)_{\text{O}}$ donors. In order to understand the doping mechanism and the acceptor levels of this dual-acceptor co-doped ZnO, further theoretical studies are required in addition to the available experimental work.

In this work, we study the mechanism of Li, N dual-acceptor co-doped p-type ZnO within the frame work of density function theory. It is found that the p-type conductivity could be obtained by Li doping under O-rich conditions, and the Li_{Zn} acceptors will dominate the p-type conductivity even in the Li, N co-doped ZnO samples.

2 Model and methodology

All the calculations in this work are carried out by the first-principles plane wave method with PAW pseudo-potential technology [6], as implemented in the VASP codes [7], with local density approximation [8, 9], Zinc $3d$ states treated as valence electrons in the PAW pseudo-potential. The energy cutoff for the plane wave expansion is 400 eV. All the atoms are allowed to relax during the calculation until the Hellmann–Feynman forces converge to less than 20 meV/Å. The optimal crystal lattice constants of ZnO ($a = 0.324$ nm, $c = 0.518$ nm) are in excellent agreement with the experimental values ($a = 0.325$ nm, $c = 0.521$ nm) with errors of only about 0.3% and 0.6% for a and c , respectively. A 32-atom supercell model is adopted for our study of Li, N co-doping in ZnO. Calculations of the formation energy for defects (Li_{Zn}^- and $(\text{Li}_{\text{Zn}}\text{-N}_{\text{O}})^-$) are done in a 72-atom supercell and a 32-atom supercell to estimate the errors from the choice of supercell. It is found that formation energy differences are about 64 meV and 110 meV for $(\text{Li}_{\text{Zn}})^-$ and $(\text{Li}_{\text{Zn}}\text{-N}_{\text{O}})^-$, respectively. It will be shown later that the relatively large errors will not affect our main conclusion. Gamma centered $4 \times 4 \times 4$ k -point mesh is employed for the Brillouin zone integration of the 32-atom supercell.

The conductivity of a doped semiconductor is determined by the concentration of defects, which depends on their formation energy. The formation energy (E^f) for a defect comprising of an atom D in the charge state q can be computed using the expression [10, 11], in the equilibrium grown condi-

✉ Fax: +86-208-7112837, E-mail: phrhyao@scut.edu.cn

tion:

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

In the first term, $E_{\text{tot}}(D, q)$ and $E_{\text{tot}}^{\text{bulk}}(\text{ZnO})$ are the total energies of ZnO with and without defect D , respectively. The second term of (1) represents the energy change due to exchange of atoms with their chemical reservoirs. μ_i is the absolute value of the chemical potential of atom i and n_i is the number of such defect atoms: $n_i = -1$ if an atom is added, while $n_i = 1$ if an atom is removed. The third term in (1) represents the energy change due to exchange of electrons with the carrier reservoir, E_{VBM} represents the energy at the VBM of the defect free system, E_F is the Fermi energy relative to the E_{VBM} . For $\text{Li}_{\text{Zn}}\text{-N}$ defect in Li, N co-doped ZnO, (1) can be defined as

$$E^f(\text{Li}_{\text{Zn}} - \text{N}_O, q) = E_{\text{tot}}(\text{Li}_{\text{Zn}} - \text{N}_O, q) - E_{\text{tot}}^{\text{bulk}}(\text{ZnO}) - \mu_{\text{Li}} - \mu_{\text{N}} + \mu_{\text{ZnO}} + q(E_F + \varepsilon_{\text{VBM}}). \quad (2)$$

Since the defect formation energies are conventionally defined with respect to the chemical potential of the elemental bulk(s), we express μ_i as $\mu_i = \Delta\mu_i + \mu_i$ (bulk) and (1) can thus be rewritten as

$$E^f(\text{Li}_{\text{Zn}} - \text{N}_O, q) = \Delta E(\text{Li}_{\text{Zn}} - \text{N}_O, q) + \Delta\mu_{\text{Li}} - \Delta\mu_{\text{N}} + \Delta\mu_{\text{O}} + \Delta\mu_{\text{Zn}} + qE_F. \quad (3)$$

Here

$$\Delta E(\text{Li}_{\text{Zn}} - \text{N}_O, q) = E_{\text{tot}}(\text{Li}_{\text{Zn}} - \text{N}_O, q) - E_{\text{tot}}^{\text{bulk}}(\text{ZnO}) - \mu_{\text{Li}}^{\text{bulk}} - \mu_{\text{N}}^{\text{bulk}} + \mu_{\text{O}}^{\text{bulk}} + \mu_{\text{Zn}}^{\text{bulk}} + q\varepsilon_{\text{VBM}}. \quad (4)$$

The atomic chemical potential should be smaller than that of the corresponding elemental bulk to avoid precipitation of the latter.

$$\Delta\mu_i \leq 0. \quad (5)$$

Meanwhile, to maintain a stable compound ZnO and to avoid other possible competing phases, it must satisfy the following conditions

$$\begin{aligned} \Delta\mu_{\text{Zn}} + \Delta\mu_{\text{O}} &= \Delta H_f^{\text{ZnO}} \\ 2\Delta\mu_{\text{Li}} + \Delta\mu_{\text{O}} &\leq \Delta H_f^{\text{Li}_2\text{O}} \\ 3\Delta\mu_{\text{Zn}} + 2\Delta\mu_{\text{N}} &\leq \Delta H_f^{\text{Zn}_3\text{N}_2} \\ 3\Delta\mu_{\text{Li}} + \Delta\mu_{\text{N}} &\leq \Delta H_f^{\text{Li}_3\text{N}}. \end{aligned} \quad (6)$$

Here ΔH_f^{ZnO} , $\Delta H_f^{\text{Li}_2\text{O}}$, $\Delta H_f^{\text{Li}_3\text{N}}$, $\Delta H_f^{\text{Zn}_3\text{N}_2}$ represent the formation energy of ZnO and corresponding possible competing phases compound. The calculated cohesive energies and the formation energies of corresponding elements and compounds in Li, N co-doped ZnO are listed in Table 1. The calculated heat of formation for ZnO (-3.93 eV) is close to the experimental value of (-3.61 eV).

Compound (element)	Space group	Formation energy (eV)
ZnO	<i>P63mc</i>	-3.93
Li ₂ O	<i>Fm-3m</i>	-6.24
Li ₃ N	<i>P63/mmc</i>	-2.45
Zn ₃ N ₂	<i>Ia-3</i>	-0.71
Li	<i>Im-3m</i>	-2.05
Zn	<i>P63/mmc</i>	-1.87
N(N ₂)	<i>P1</i>	-8.74
O(O ₂)	<i>P1</i>	-4.80
NO	<i>P1</i>	0.72

TABLE 1 The cohesive energies of elements and the formation energies of possible competing compounds in Li, N co-doped ZnO, as well as their space group

3 Results and discussion

3.1 The p-type conductivity of single Li or N doped ZnO

It is widely accepted that group-I elements are good dopants for p-type ZnO in regard to their shallow defect energy levels from theoretical calculations [12, 13]. In particular, Li may have high solubility in ZnO due to the weak repulsion between the Li substitution defects [12]. Moreover, the defect levels of Li substitution are expected to be shallower than those from the other group I elements, such as Na, K. Unfortunately, theoretical calculations in [12, 14] concluded that Li_{Zn} acceptors are mostly self-compensated by Li_i interstitial donors under both extremely Zn-rich and O-rich condition. This becomes the dominant fact for the difficulty of p-type ZnO by Li doping, while the compensation from the intrinsic defects (such as V_O and Zn_i) plays a less important role. However, experimentally, good p-type electrical properties were successfully observed [15–17] in single Li doped ZnO. Furthermore, the dependence of p-type conductivity on the growth temperature, annealing temperature and the concentration of Li dopant was investigated in the earlier experimental work [15–17].

In this work, the formation energies of Li_i , Li_{Zn} and $\text{Li}_i\text{-Li}_{\text{Zn}}$ are shown in Fig. 1. We find that Li_{Zn} acceptor is compensated by Li_i interstitial under the extremely Zn-rich condition, which is in consistent with the results in the literature [12, 14]. However, under the extremely O-rich condition, the formation energy of Li_{Zn}^- acceptor is lower than the interstitial Li_i^+ by 1.25 eV at the VBM, which means that Li doped p-type ZnO could be obtained under the O-rich condition. This is consistent with the experimental observation. The disagreement between this work and earlier theoretical work may be largely due to the different calculated value of the heat formation for ZnO (-2.89 eV in [12] vs. -3.93 eV in this work). We have carefully checked our calculation on ΔH_f^{ZnO} , and find our value is close to experimental values (-3.61 eV) and that from other theoretical work (-3.44 eV) [14]. When the chemical potential of O is chosen as $\frac{1}{2}\Delta H_f^{\text{ZnO}}$ or less, it shows that Li_{Zn} acceptor could be compensated by Li_i interstitial or $\text{Li}_i\text{-Li}_{\text{Zn}}$ complex donors, which is consistent with [18]. Figure 2 shows the dependence of the formation energy of Li_{Zn} , Li_i and $\text{Li}_i\text{-Li}_{\text{Zn}}$ on the chemical potential of O. The maximum chemical potential of Li is used here under the restriction of (5) and (6). It indicates that: when $\Delta\mu_{\text{O}} < -1.3$ eV, Li_{Zn} , the acceptor is compensated by Li_i interstitial; when $-1.3 \text{ eV} < \Delta\mu_{\text{O}} < -1.2$ eV, Li_{Zn} , the acceptor is compen-

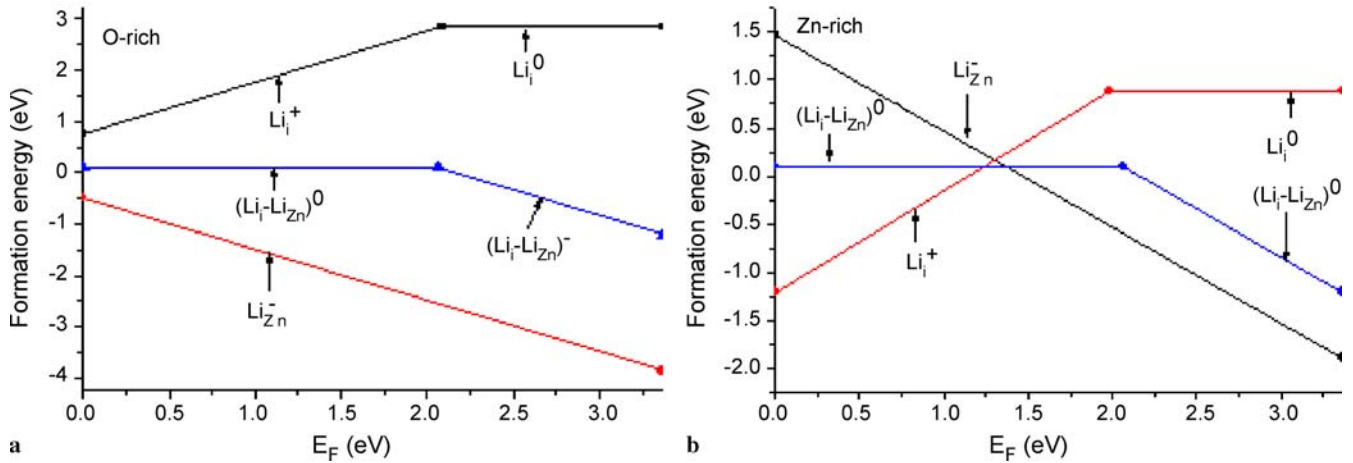


FIGURE 1 The formation energies of Li_{Zn} , Li_i and $\text{Li}_i\text{-Li}_{\text{Zn}}$ as a function of the Fermi energy (E_F) under (a) O-rich, and (b) Zn-rich conditions. The maximum chemical potential of Li (i.e. $\Delta\mu_{\text{Li}} = -3.12$ eV) is adopted here with the restriction from (5) and (6). The *solid dot* denotes the defect transition energies

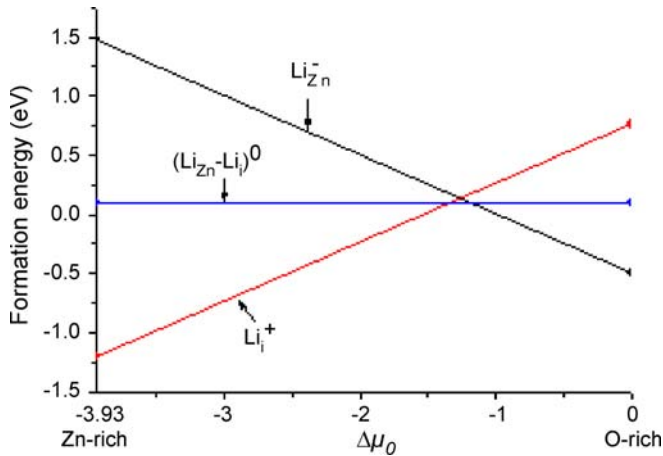


FIGURE 2 Dependence of the formation energy of Li_{Zn} , Li_i and $\text{Li}_i\text{-Li}_{\text{Zn}}$ on the chemical potential of O. The maximum chemical potential of Li is adopted here with the restriction from (5) and (6). $\Delta\mu_{\text{O}} = -3.93$ eV corresponds to the extremely Zn-rich condition, while $\Delta\mu_{\text{O}} = 0$ eV corresponds to the extremely O-rich condition

sated by neutral $\text{Li}_i\text{-Li}_{\text{Zn}}$ complex; when $\Delta\mu_{\text{O}} > -1.2$ eV, the formation energy of Li_{Zn} is the lowest among them. Since the formation energy of $\text{Li}_i\text{-Li}_{\text{Zn}}$ increases twice as fast as Li_{Zn} , Li_i when $\Delta\mu_{\text{Li}}$ decreases, the compensating effect from $\text{Li}_i\text{-Li}_{\text{Zn}}$ would be weakened as $\Delta\mu_{\text{Li}}$ decreases.

Among group-V elements, N was considered as the best p-type ZnO dopant due to its small atomic size, but the N_{O} defect may not to be stable. The donor defect $(\text{N}_2)_{\text{O}}$ may be more stable due to the strong binding energy of N_2 . Furthermore the acceptor level of N is deep and it is difficult to ionize. We can calculate the formation energy of N_{O} acceptor for N doped ZnO. According to (1) and (2), the defect formation energy depends on the Fermi energy (E_F) and the chemical potential of elements in the equilibrium growth conditions. The defect formation energy decreases with the increase of chemical potential dopant elements (Li or N), and the decrease of chemical potential of elements to be substituted (Zn or O). Since the cohesive energy of N_2 is large, the chemical potential of N_2 is very low. As a result, the formation energy of N_{O} is

still very high even if under the extremely N-rich and Zn-rich condition, which is difficult for the p-type ZnO.

Figure 3 shows the dependence of the formation energy of N_{O} acceptor on the Fermi energy (E_F). In the extremely Zn-rich ($\Delta\mu_{\text{O}} = -3.93$ eV) and O-rich conditions ($\Delta\mu_{\text{O}} = 0$), the formation energy of N_{O} is 1.06 eV, 4.99 eV respectively. The high formation energy indicates that it is difficult to form the N_{O} acceptor with N_2 as the dopant. This is consistent with the experimental observation of n-type conductivity in N doped ZnO using normal N_2 as the dopant. The defect formation can be decreased significantly by expanding the physically accessible range of the dopant atomic chemical potentials. This can be done by using either epitaxial growth techniques such as MBE, or meta-stable molecules as doping sources. Good p-type conductivity of ZnO has been achieved by using meta-stable molecules (NO , N_2O) as doping sources [19, 20]. Using the meta-stable molecule NO as doping sources, (satisfying $\Delta\mu_{\text{N}} + \Delta\mu_{\text{O}} \leq \Delta H_{\text{f}}^{\text{NO}} = 0.720$ eV), we can calculate the formation energy of N_{O} in N doped ZnO. Figure 3 shows the difference of the formation energy of N_{O} by using NO and N_2 as the dopant. We find that the formation energy of N_{O} is reduced by 4.65 eV in the Zn-rich condition ($\Delta\mu_{\text{N}} = 4.65$ eV) and 0.72 eV in the O-rich condition ($\Delta\mu_{\text{N}} = 0.72$ eV) by using NO as the dopant, which is in agreement with the conclusions from [23]. The acceptor level of N_{O} lies at 0.437 eV above the VBM, consistent with the result from earlier works in [12, 21, 22]. It also indicates that Zn-rich is a better condition for the formation of N_{O} acceptor.

3.2 The mechanism of Li, N dual-acceptor codoped p-type ZnO

Based on the discussion of Sect. 3.1, we find that the optimal condition for p-type Li doping ZnO is the O-rich condition, while the optimal condition for p-type N doping ZnO is the Zn-rich condition. There should be an optimal growth condition for the Li, N co-doped p-type ZnO to balance both Li and N doping. Actually, the p-type Li, N co-doped ZnO was prepared in experiments [2–5], and the best p-type electrical properties with resistivity of 0.93 Ω cm,

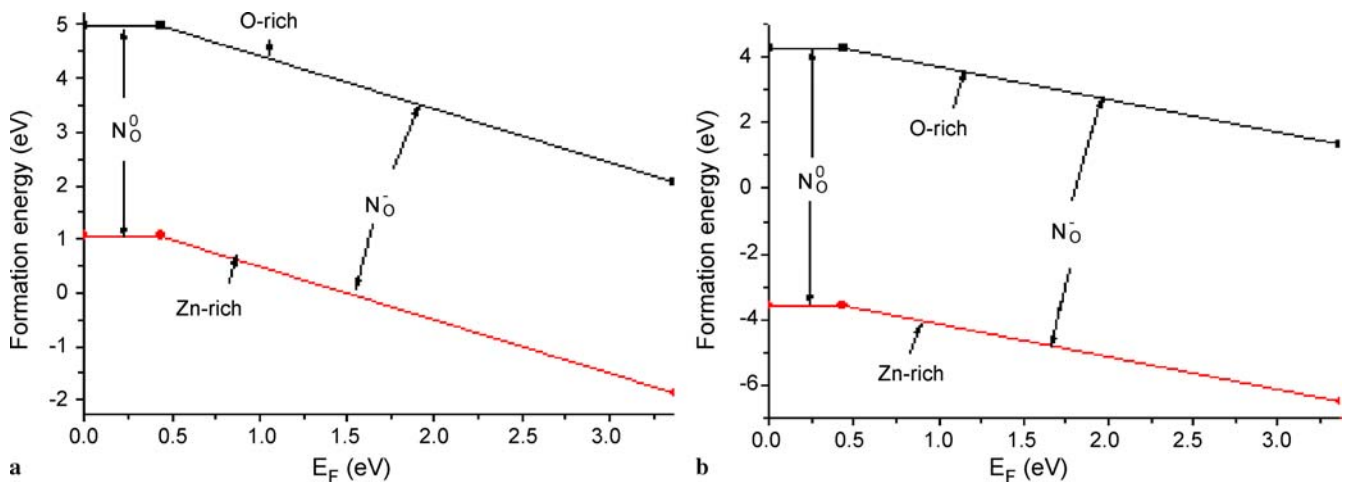


FIGURE 3 Dependence of the formation energy of N_O acceptor on the Fermi energy (E_F) under both the O-rich and Zn-rich conditions with (a) normal N_2 and (b) NO as the source of N dopant

Hall mobility of $0.75 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$, and carrier concentration of $8.92 \times 10^{18} \text{ cm}^{-3}$. The experimental results [2, 3] indicate that the p-type conductivity of $\text{ZnO}:(\text{Li}, \text{N})$ films is remarkably improved, and its stability is also improved in comparison with single Li or N doped samples. It was suggested in [4, 5] that the p-type conductivity of the $\text{ZnO}:(\text{Li}, \text{N})$ could be attributed to the formation of $\text{Li}_{\text{Zn}}-\text{N}_O$ complex acceptor. However, it is easy to expect that the repulsive interaction between Li_{Zn} acceptors and N_O acceptors could keep them apart from each other. To understand how the impurities of Li and N coexist in the co-doped ZnO, the formation energies of various Li, N defect complex are calculated here.

For p-type ZnO co-doped with Li, N ($\text{ZnO}:(\text{Li}, \text{N})$), we replace one of the 16 sites of Zn atoms by an Li atom, and replace one of the 16 sites of O atoms by an N atom. Li and N atoms lie at the nearest-neighbour sites in wurtzite ZnO. The Li-N pair could be along the c axes, or in the hexagonal plane. The total energy difference is only 0.086 eV between the two configurations, so we do not distinguish them in the following discussion. Figure 4 shows the dependence of the formation energy of $\text{Li}_{\text{Zn}}-\text{N}_O$ complex and Li_{Zn} , N_O single acceptor on the Fermi energy. When N_2 is used as the dopant source, the formation energy of Li_{Zn} acceptor is always lower than that of N_O and the defect complex under the extremely O-rich condition. This is also true under the extremely Zn-rich condition except that E_F is close to VBM. Thus, the concentration of Li_{Zn} acceptor must be higher than the $\text{Li}_{\text{Zn}}-\text{N}_O$ dual acceptor. It means that the $\text{Li}_{\text{Zn}}-\text{N}_O$ dual acceptor is not the dominative p-type conducting source in Li, N co-doped ZnO, but the good p-type electrical property is mainly attributed to the Li_{Zn} acceptor, especially under the O-rich condition. The relative concentration of N_O acceptor increases as $\Delta\mu_{\text{Zn}}$ increases. If using the meta-stable molecule NO as the N dopant source (Fig. 4c and d), the formation energy of N_O acceptor is lower than the other Li, N related defects in the extremely Zn-rich condition, although the Li_{Zn} acceptor is still the lowest in the extremely O-rich condition. It also indicates that $\text{Li}_{\text{Zn}}-\text{N}_O$ dual acceptor is not the dominative p-type conductivity source in Li, N co-doped ZnO.

To see whether the defect complex $(\text{Li}_{\text{Zn}}-\text{N}_O)$ can form, we calculate the defect complex binding energy as

$$E_b[(\text{Li}_{\text{Zn}}-\text{N}_O)^Q] = H_f(\text{Li}_{\text{Zn}}, q_1) + H_f(\text{N}_O, q_2) - H_f(\text{Li}_{\text{Zn}}-\text{N}_O, q_1 + q_2), \quad (7)$$

where $Q = q_1 + q_2$. When multiple combinations of (q_1, q_2) are available for the total charge of the complex, Q , the combination with lower energy is referred to. For example, the binding energy of complex $(\text{Li}_i-\text{N}_O)^0$ is referred to as Li_i^+ and N_O^- rather than $\text{Li}_i^0-\text{N}_O^0$, since the former combination of single defects has a lower energy.

The stability of the defect complex is reflected by the defect binding energy (E_b). The positive E_b indicates that the defect pairs are stable, while the negative E_b means the defect pairs do not tend to form. Here the binding energy of a complex does not depend on the Fermi level since the $q(E_{\text{VBM}} + E_F)$ term for formation energy is cancelled out, assuming the VBM is unchanged in the defect host. The calculated binding energies for $(\text{Li}_{\text{Zn}}-\text{N}_O)^{2-}$, $(\text{Li}_{\text{Zn}}-\text{N}_O)^-$, and $(\text{Li}_{\text{Zn}}-\text{N}_O)^0$ are -0.52 eV , -0.25 eV and -0.47 eV respectively, indicating that the defect pair is unstable with respect to the isolated defects. This indicates that the dual-acceptor complex $\text{Li}_{\text{Zn}}-\text{N}_O$ is unlikely to form in Li, N co-doped ZnO, inconsistent with expectation of the $\text{Li}_{\text{Zn}}-\text{N}_O$ complex from [4, 5]. The negative binding energy of the $\text{Li}_{\text{Zn}}-\text{N}_O$ complex could be understood from the repulsive interaction between Li_{Zn} acceptors and N_O acceptors. The level interaction between the acceptor levels of Li_{Zn} and N_O is very weak [24], since they have different wave function characters and symmetry. However, the calculated $(\text{Li}_i-\text{N}_O)^0$ and $(\text{Li}_i-\text{Li}_{\text{Zn}})^0$ binding energy is 0.18 eV , 0.17 eV respectively. It indicates that these defect pairs tend to form in the ZnO sample. As a result, the formation of Li_i-N_O could reduce the concentration of isolated interstitial Li_i defects, and thus reduce its compensation effect under certain growth condition.

Figure 5 shows the dependence of the formation energy of Li_i and Li_i-N_O on the Fermi energy. The formation energy of donor-acceptor complex $(\text{Li}_i-\text{N}_O)^0$ is much higher than the interstitial Li_i under all ranges of E_F under the extremely O-rich condition. Under the extremely Zn-rich condition, the formation energy of $(\text{Li}_i-\text{N}_O)^0$ is much lower than Li_i . This indicates that the additional introduc-

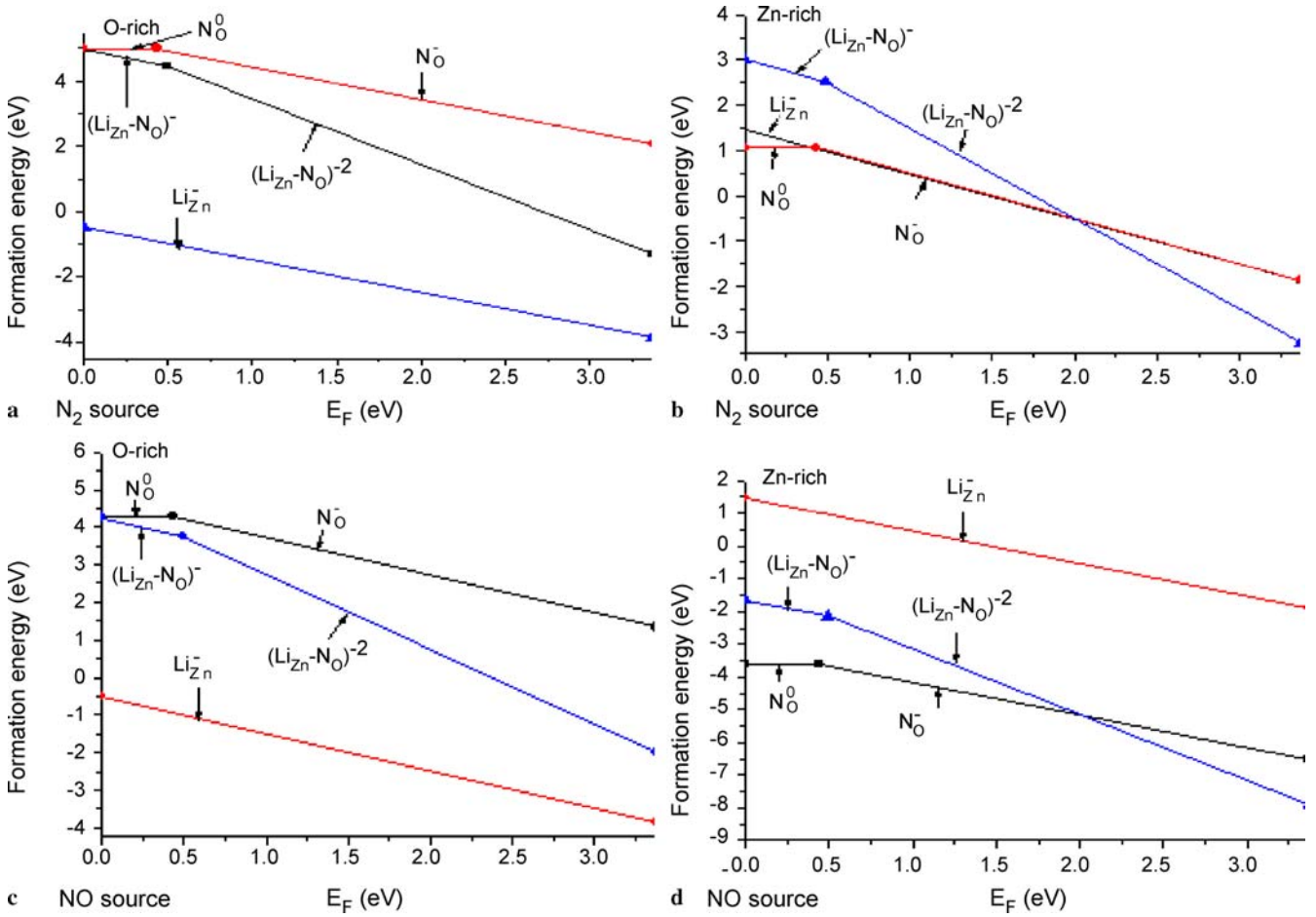


FIGURE 4 Dependence of the formation energy of $Li_{Zn}-N_O$ complex dual acceptor and the single Li_{Zn} , N_O acceptor on the Fermi energy (E_F). The maximum chemical potential of Li is used with the restriction of (5) and (6) under (a) O-rich, and (b) Zn-rich conditions with N_2 as the N dopant source, and under (c) O-rich, and (d) Zn-rich conditions with NO as the N dopant source

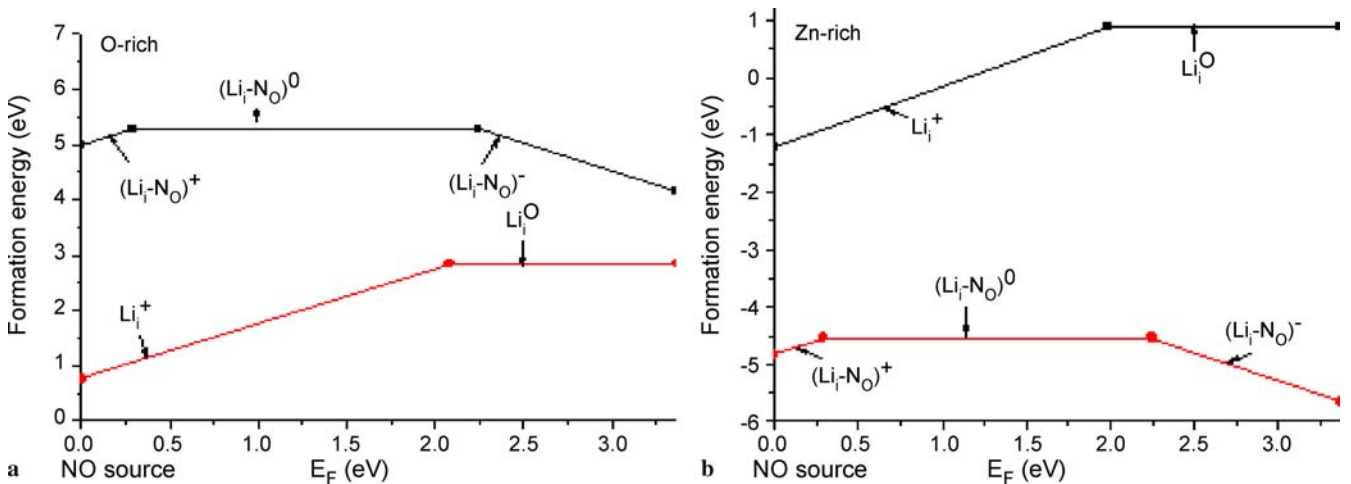


FIGURE 5 Dependence of the formation energy of Li_i and Li_i-N_O on the Fermi energy. The maximum chemical potential of Li is used with the restriction of (5) and (6), with NO as the N dopant. Plots (a) and (b) are under the O-rich, and Zn-rich conditions, respectively

tion of N may help compensate the Li_i donor defects significantly under the Zn-rich condition. However, this will not turn ZnO into p-type under the Zn-rich condition, and thus the role of codoping N remains to be clarified for the p-type conductivity in ZnO even though NO is used as the N source.

4 Conclusion

In conclusion, the formation of various defects and defect complexes were studied in a Li, N doped ZnO sample, by calculating their defect formation energies and binding energies. It was demonstrated that p-type conductivity could be

achieved by Li doping under the O-rich condition. The p-type conductivity in Li, N doped ZnO will still be dominated by the Li_{Zn} defects. The dual-acceptor complex $\text{Li}_{\text{Zn}}\text{-N}_{\text{O}}$ is unlikely to form due to their repulsive interaction. The additional introduction of N may help to compensate for the single Li_i donor defects under the Zn-rich condition, but its role in the p-type conductivity remains to be clarified.

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