

***p*-Type Conductivity in N-Doped ZnO: The Role of the N_{Zn} - V_O Complex**

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Although nitrogen-doped zinc oxide has been fabricated as a light-emitting diode, the origin of its *p*-type conductivity remains mysterious. Here, by analyzing the surface reaction pathway of N in ZnO with first-principles density functional theory calculations, we demonstrate that the origin of *p*-type conductivity of N-doped ZnO can originate from the defect complexes of N_{Zn} - V_O and N_O - V_{Zn} . Favored by the Zn-polar growth, the shallow acceptor of N_O - V_{Zn} actually evolves from the double-donor state of N_{Zn} - V_O . While N_{Zn} - V_O is metastable, the *p*-doping mechanism of N_{Zn} - $V_O \rightarrow N_O$ - V_{Zn} in ZnO will be free from the spontaneous compensation from the intrinsic donors. The results may offer clearer strategies for doping ZnO *p*-type more efficiently with N.

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As a well-known II-VI semiconductor, ZnO with the direct band gap of 3.37 eV at room temperature has a large exciton binding energy of 60 meV [1]. In comparison, GaN, with almost the same band gap, shows the exciton energy at about 20 meV [2]. Due to its large exciton energy, ZnO has been taken as a promising material to fabricate ultraviolet (UV) light emitters [3,4]. But, it suffers notoriously the doping asymmetry problem [5–7], i.e., it can be easily doped *n*-type but not *p*-type. Unlike GaN, whose light-emitting diodes (LEDs) and laser diodes have been successfully fabricated and commercialized, the optoelectronic application of ZnO has been hindered by lack of a practical and efficient *p*-doping method. While the quality of *p*-doping indeed decides the future of ZnO as a UV light-emitting material, in recent years great research efforts have been made to achieve sufficient *p*-type doping in ZnO, where acceptors are basically introduced with N [8,9], P [10], Sb [11], As [12], etc. Among those acceptor elements, N may be the best candidate for *p*-doping ZnO since it has the similar atomic radius and electronegativity as O [13]. Typically, for molecular beam epitaxy (MBE) growth, N-doping has been employed to fabricate *p*-type ZnO films by many groups. In 2002, Look *et al.* got the N-doped *p*-type ZnO layer with the hole concentration of $9 \times 10^{16} \text{ cm}^{-3}$ by MBE on an Li-diffused semi-insulating ZnO substrate [8]. In 2005, Tsukazaki *et al.* achieved *p-i-n* homojunction violet LEDs from the MBE-grown N-doped ZnO films on ScAlMgO_4 substrate, with a hole concentration of about $1 \times 10^{16} \text{ cm}^{-3}$ at 300 K [9]. In 2006, ZnO *p-n* junction LEDs were well fabricated on Al_2O_3 substrates by plasma-assisted MBE [14,15]. Moreover, in 2010, the UV electroluminescence emission was demonstrated on the N-doped $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0.1 \leq x \leq 0.4$)

films grown on the Zn-polar ZnO substrates by MBE [16]. Last year, MgZnO:N/ZnO/MgZnO double heterostructure UV LEDs were also fabricated with N-doped MgZnO layers [17].

However, despite the fact that UV LEDs have been successfully fabricated by N-doped ZnO materials, the origin of their *p* conductivity remains puzzling. In principle, the working of LEDs means N atoms bring shallow acceptors into ZnO. Experimentally, Look *et al.* assigned a photoluminescence line at 3.238 eV to a donor-acceptor transition, which suggests an estimated acceptor ionization energy of 170–200 meV [8]. But, the shallow acceptor nature of N in ZnO has not been supported by the theoretical studies. In 2001, based on the density functional theory (DFT) within the local-density-functional approximation (LDA), Lee *et al.* studied N-related defects and found only the O-site N (N_O) is an acceptor [18]. They indicated that N acceptors in ZnO are greatly compensated by N_2 molecules at oxygen sites and N-acceptor- N_2 complexes [18]. In 2002, with the LDA method, Park *et al.* suggested the defect level of substitutional N_O in ZnO is 0.4 eV [19]. In 2006, Li *et al.* reported their LDA calculation result that the $(0/-)$ transition energy level of N_O is 0.31 eV [20]. As DFT-LDA calculations underestimate band gaps, it is argued that such results may bring large uncertainties in describing the defect levels in wide-band-gap materials [21]. In 2009, based on hybrid functional calculations, Lyons *et al.* found that N_O is actually a deep acceptor with an exceedingly high ionization energy of 1.3 eV and hence concluded that nitrogen cannot lead to hole conductivity in ZnO [21]. While little information on the chemical environment of N atoms in ZnO has been collected from experimental observations [8,9,14–17], the

inconsistency between experimental and theoretical results cannot be solved. In fact, without a clear physics picture of the p -type conductivity in N-doped ZnO, it would be aimless to optimize its light-emitting performance. In this Letter, we demonstrate that the p -type nature of N-doped ZnO can originate from the defect complex composed of substitutional N_O and zinc vacancy V_{Zn} by analyzing its dynamic growth process. The N_O - V_{Zn} complex actually comes from the metastable donor defect of N_{Zn} - V_O , thus its p -type doping can survive the compensation during MBE growth. Considering the surface reaction pathway of N_{Zn} - V_O defects, we suggest the possible ways to achieve better p -type ZnO.

To our best knowledge, the theoretical studies so far regarding the electronic behaviors of N-doped ZnO are based on the bulk model simulations [5–7,18–21], where the dynamic MBE growth process has not been taken into consideration. In fact, although wurtzite ZnO (w -ZnO) has distinctly two polar faces of Zn and O, typically only the Zn one is preferred to grow high-quality p -type ZnO with nitrogen during MBE processes [16,17]. That hints it may be the right way to bridge the gap between theoretical analysis and experimental observation of N-doped ZnO by simulating its dynamic growth process with polar surface dependence. Our first-principles calculations are based on DFT within Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [22] and the projected augmented wave (PAW) method [23–26]. When necessary, the hybrid functional calculation containing a mix of the exact exchange (36%) [21] and the PBE functional have been employed to calibrate the band gap of ZnO to its experimental value. The cutoff energy for the plane-wave basis set is 400 eV and the Brillouin zone is sampled with the kpoint separation $<0.04 \text{ \AA}^{-1}$. The experimental lattice parameters of ZnO at 4.2 K ($a = 3.248 \text{ \AA}$, $c = 5.203 \text{ \AA}$) [27] are used in building the structural models, where the atomic positions are relaxed until their residual forces are less than 0.01 eV \AA^{-1} .

The absorption energies of N and O atoms absorbed on the Zn-polar surfaces of ZnO are calculated to understand their surface growth mechanism. We consider a 4×4 periodic slab geometry to represent the Zn-polar w -ZnO. The unit cell contains an atomic slab with eight(nine) atomic ZnO layers for the Zn-(O-) terminated surface and a vacuum region of larger than 15 \AA . The bottom O layer of the slab is saturated with H atoms as shown in Fig. 1(a). Four possible absorption sites of N or O adatoms on the surface layers as shown in Figs. 1(b)–1(e) are selected to compare their absorption energies. During structural relaxation, the atomic positions of two bottom Zn and O layers are fixed. The absorption energy E_{abs} can be defined as:

$$E_{\text{abs}} = E_{\text{slab}+X}^{\text{tot}} - E_{\text{slab}}^{\text{tot}} - \mu_X. \quad (1)$$

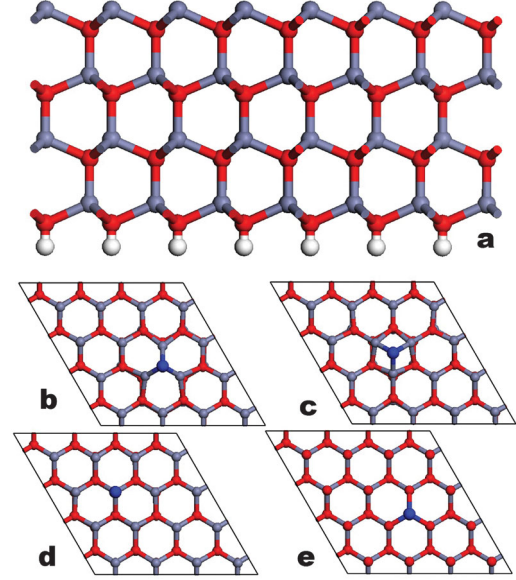


FIG. 1 (color). Side view of the periodic slab to represent the Zn-polar ZnO (a), the adsorption sites of hcp (b), fcc (c), and on-top (d) on Zn surface layer, and the adsorption site of hcp (e) on O surface layer. The gray, red, blue, and white balls represent Zn, O, N, and H atoms, respectively.

Here, $E_{\text{slab}+X}^{\text{tot}}$ is the total energy of the slab with a X adatom, $E_{\text{slab}}^{\text{tot}}$ is the total energy of the slab, and μ_X accounts for the chemical potential of adatom X . If μ_N is set to the energy per atom calculated for N_2 , we have the absorption energy of the Zn surface as listed in Table I. We can see that N atoms have much higher absorption energy than O atoms at each possible high-symmetry site of the Zn surface. That indicates N atoms are not easy to attach to the Zn surface during the MBE growth of ZnO. However, for N at the hcp site of the Zn-polar O surface, i.e., N_{Zn} as shown in Fig. 1(e), its absorption energy is rather low at just 0.08 eV. Thus, as N atoms grow on the Zn-polar ZnO by MBE, they indeed prefer to form the Zn-site defects of N_{Zn} instead of the O-site ones of N_O . On the contrary, N_{Zn} is dynamically unfavored if growing on the O-polar O surface, as it stays at the on-top site bonding to only one surface O atom. That may result in a NO molecule, free from the surface bonding. The calculated formation enthalpies of ZnO, O_2 , and N_2 by PBE and their experimental values are listed in Table II, which suggest the PBE method may provide $\sim 94\%$ accuracy in describing the formation energies of N-doped ZnO structures.

TABLE I. Calculated absorption energy (in eV) of N and O at the high-symmetry sites of the Zn-polar Zn surface of ZnO.

	hcp	fcc	On-top
O(Zn-rich)	0.25	1.02	2.58
O(O-rich)	-3.16	-2.39	-0.83
N	1.36	1.90	4.14

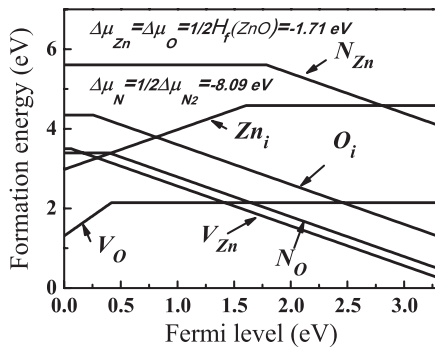
TABLE II. Calculated formation enthalpy (in eV) of ZnO, O₂, and N₂ by PBE and their experimental values.

	PBE	Expt
ZnO	3.41	3.61 [28]
O ₂	5.65	5.25 [29]
N ₂	10.38	9.89 [29]

At the first glance, the formation of N_{Zn} instead of N_O seems against the common sense that N should stay at the sites of anions. For a defect with charge q (X^q) in bulk ZnO, the formation energy $E(X^q)$ is defined as

$$E(X^q) = E_{\text{tot}}(X^q) - E_{\text{tot}} - \sum n_i \mu_i + q(E_F + E_v + \delta V). \quad (2)$$

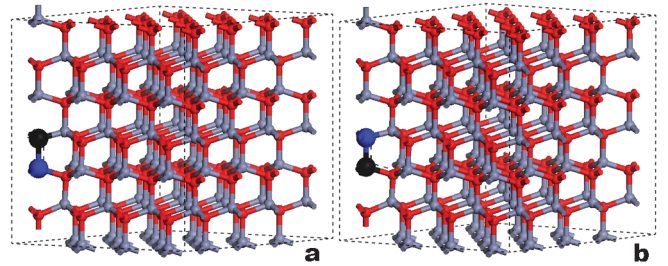
Here, $E_{\text{tot}}(X^q)$ is the total energy of the supercell with some defect; E_{tot} is the total energy of the equivalent bulk ZnO supercell; n_i and μ_i are the atomic number and chemical potential of the species i ; E_F is the Fermi level; E_v is the valence band maximum (VBM); and δV represents the potential shift between supercells. If simulated by the 192-atom (443) supercells of w -ZnO, the formation enthalpies of the defects can be plotted as functions of the Fermi level of E_F , as shown in Fig. 2. If under the neutral condition of $\Delta\mu_{\text{Zn}} = \Delta\mu_{\text{O}} = \frac{1}{2}H_f(\text{ZnO}) = -1.71$ eV, N_{Zn} in bulk indeed has a higher formation energy than N_O. As two competitive processes, whether N_{Zn} or N_O dominates the MBE process relies on the growth condition. As N_{Zn} and N_O occupy the opposite sites of Zn and O, their formation energies in bulk ZnO depend reversely upon μ_{Zn} or μ_{O} . That is N_{Zn} (N_O) in bulk ZnO has the lower formation energy under the O (Zn)-rich condition. However, that the Zn-polar growth N_{Zn} has a lower surface absorption energy than N_O gives it an advantage initially to form during the layer-by-layer growth. As to μ_{N} , both formation energies of N_{Zn} and N_O decrease with it from Eq. (2). In this manner, it is desirable to use NO or NO₂ as

FIG. 2. Calculated PBE defect formation enthalpies as functions of the Fermi level E_F .

the doping source instead of N₂ [30] together with the plasma enhanced technique for MBE growth.

For a clearer understanding of the reaction path of N_{Zn}, the role of surface morphology of ZnO should be discussed as well. Obviously, N adatoms experience different bonding sequences following the surface polarity. On the Zn-polar surface, N_{Zn} has three neighbor O atoms to bond. Whereas on the O-polar one, N_{Zn} can bond to only one O atom below. While fixed by two more N-O bonds, N_{Zn} on the Zn polar surface gets much more chance to survive the competition from Zn. Furthermore, during the Zn-polar growth, the coming O atoms sit just above the Zn atoms, rather than bonding three Zn atoms on the reverse polar face. For lower energy, the falling O atom will circumvent the N_{Zn} anion to bond to its neighbor Zn cations, and that results in a vacancy (V_{O}) on top of N_{Zn}, as shown in Fig. 3(a). Otherwise, after forming a NO molecule and free from the surface bonding, they will leave a Zn vacancy (V_{Zn}), the intrinsic acceptor. In fact, N or Zn may also exist on top of N_{Zn}, forming defect complexes of N_{Zn}-N_O or N_{Zn}-Zn_O, respectively. As contributing no carriers, the trivial defect complex of N_{Zn}-N_O (N₂) will be neglected. The unstable complex of N_{Zn}-Zn_O will degenerate into the well-studied defect of N_O. As acceptors, V_{Zn} and N_O suffer the compensation from the intrinsic donors.

Figure 3(a) draws the 192-atom (443) w -ZnO supercell containing a N_{Zn}- V_{O} complex. Such a complex may not be at the energy minimum, as it will evolve into the N_O- V_{Zn} complex if N_{Zn} jumps to its neighbor vacancy of O as shown in Fig. 3(b). To understand the thermal stability, the minimum energy path and energy barrier of from N_{Zn}- V_{O} to N_O- V_{Zn} has been identified with the elastic band method as plotted in Fig. 4. The simulated minimum energy path indicates the N_{Zn}- V_{O} complex is a metastable configuration with ~ 0.5 eV higher per supercell than N_O- V_{Zn} . While the energy barrier to N_O- V_{Zn} is more than 1.1 eV, the N_{Zn}- V_{O} complex would survive the MBE growth of mild temperature. As a double donor, the formation of N_{Zn}- V_{O} will not trigger the spontaneous formation of intrinsic compensating defects in ZnO [31] as acceptors do. If activated after the epitaxy growth, the

FIG. 3 (color). ZnO supercells with the N_{Zn}- V_{O} complex (a) and the N_O- V_{Zn} complex (b). The grey, red, blue, and black balls represent Zn, O, and N atoms and vacancy respectively.

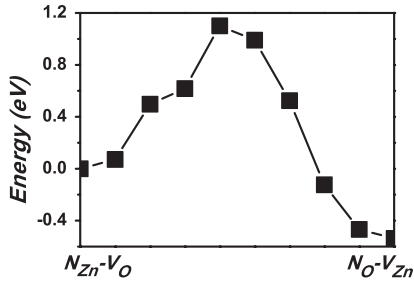


FIG. 4. Calculated minimum energy path from $N_{Zn}-V_O$ to N_O-V_{Zn} with the elastic band method.

transformed acceptor of N_O-V_{Zn} would overcome self-compensation consequently with higher p -type conductivity in ZnO.

By examining the transition energy level $\varepsilon(0/-)$ of defects in ZnO, we find N_O-V_{Zn} is a shallow acceptor. Here, $\varepsilon(q/q')$ is defined as the Fermi-level position for which the formation energies of charge states q and q' are equal. The calculated $\varepsilon(0/-)$ of N_O is 0.40 eV that agrees with the published DFT results [18–20]. In comparison with that of N_O , the calculated $\varepsilon(0/-)$ of N_O-V_{Zn} , 0.11 eV is almost three times smaller. For PBE may underestimate the acceptor energy levels as well as $\varepsilon(0/-)$ as the case of N_O [21], the electronic states of N_O-V_{Zn} have also be examined by the hybrid functional method. The hybrid functional results based on the (332) w -ZnO supercells indicate that the lowest acceptor state of N_O-V_{Zn} stays 0.23 eV above VBM and its corresponding $\varepsilon(0/-)$ is 0.16 eV [32]. Therefore, the nature of double acceptor of N_O-V_{Zn} in ZnO has been confirmed shallow. Moreover, the calculated acceptor level of N-doped ZnO agrees with its experimental value, which has been reported to be about 135 meV from electrical measurements [33] and 150–210 meV from photoluminescence data [33,34].

In conclusion, the p -type conductivity of N-doped ZnO can originate from the defect complex of N_O-V_{Zn} that is a shallow acceptor. N_O-V_{Zn} actually evolves from the metastable double donor of $N_{Zn}-V_O$ that is favored by the Zn-polar growth. While the energy barrier from $N_{Zn}-V_O$ to N_O-V_{Zn} is as high as 1.1 eV, the p -doping of N_O-V_{Zn} may survive the spontaneous self-compensation from intrinsic donors in ZnO. The reaction pathway of $N_{Zn}-V_O \rightarrow N_O-V_{Zn}$ may lead to some strategies for more efficient p -doping in ZnO. They are as follows. (i) The Zn-polar growth should be selected. (ii) Plasma assisted sources of NO or NO_2 rather than pure N_2 would be desirable to increase the upper limit of μ_N for the higher N concentration. (iii) The Zn-polar growth condition has to balance between the Zn-rich and the O-rich. While the Zn-rich favors V_O on top of N_{Zn} , more oxygen would be better for less intrinsic donors. (iv) As by the nonequilibrium growth, the N-doped samples containing $N_{Zn}-V_O$ complexes could be n -type, and they need to be activated to p -type for higher p conductivity. This also means it is

advisable not to throw away a seemingly n -type sample unless it fails the LED test.

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