

Codoping of aluminum and gallium with nitrogen in ZnO: A comparative first-principles investigation

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We perform first-principles density-functional theory calculations to investigate the atomic structures and electronic properties of dopant complexes involving Al, Ga, and N in wurtzite ZnO. We find that both Al and Ga substituted on Zn sites act as single donors and exhibit a strong attractive interaction with a nitrogen acceptor located at the nearest-neighbor oxygen site in the same (0001) plane, forming passive (Al-N) and (Ga-N) complexes. These structures induce fully occupied defect states above the valence-band maximum of bulk ZnO. On introducing a higher concentration of nitrogen, (Al-2N) and (Ga-2N) complexes form. The additional N atom in these complexes prefers to occupy another nearest-neighbor site of the Al or the Ga atom, compared to being further away from it, and acts as an acceptor with ionization energies of 0.17 and 0.14 eV, respectively. These values are lower than the ionization energy of the single N acceptor, which is 0.33 eV. This indicates that (Al,N) and (Ga,N) codoping could increase the percentage of N dopants that are activated by ionization. The interaction between two (Al-N) complexes and the interaction between the (Al-2N) complex and a N atom (on a neighboring oxygen site) are very weak, indicating that the N concentration cannot be significantly increased by Al and N codoping or cluster doping. In contrast, two (Ga-N) complexes prefer to bind together in the same (0001) plane, implying that the passive complexes which create the impurity band could reach high concentration. The formation energy for (Ga-2N) is lower than (Al-2N) in the neutral and the negative charge states under most experimental conditions. Furthermore, the (Ga-2N) complex binds with additional N atoms located at nearest-neighbor O sites and therefore has a tendency to form clusters of (Ga-3N) and (Ga-4N). Under Zn-rich conditions and for an NO source of nitrogen, the cluster (Ga-3N) has a lower formation energy and lower transition levels compared to the (Ga-2N) complex; the (Ga-4N) complex has the lowest formation energy and the lowest (0/1-) transition energy among the (Ga,N) complexes. Our findings suggest that codoping of (Ga,N) could efficiently enhance the N dopant solubility with the NO source (rather than an N₂ source for nitrogen) and is likely to yield better *p*-type conductivity than (Al,N) codoping.

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I. INTRODUCTION

Zinc oxide is a promising optoelectronic material which can be utilized for blue and ultraviolet light emitting diodes, laser diodes, and solar cells due to its wide band gap of 3.2 eV (Ref. 1) and its large exciton binding energy of 60 meV at room temperature.² It has been suggested that undoped ZnO is *n* type due to a large number of intrinsic defects such as oxygen vacancies (V_O) and Zn interstitials (Zn_i).³ The obstacle that prevents full utilization of ZnO as a novel optoelectronic material is the inability of obtaining *p*-type conductivity with high hole concentration and low resistivity. In an attempt to overcome this, a variety of elements such as group-V elements (N, P, and As) on O sites or group-I elements (Li, Na, and K) on Zn sites have been studied as potential dopants.⁴⁻⁶ Theoretically, group-I elements substituting on Zn sites are shallow acceptors, but instead these dopants tend to occupy the interstitial sites, partly due to their small atomic radii, and therefore act mainly as donors.⁶ Of the group-V elements, it has been proposed that N is the most suitable dopant because it has about the same ionic radius as O, and thus should readily substitute on O sites, although theory suggests some difficulties in achieving a shallow acceptor level.⁵ Indeed, it remains difficult to achieve good quality *p*-type conduction in N-doped ZnO either due to a low dopant solubility⁶ or a high defect ionization energy.^{5,7}

One way to achieve a good solubility of N in ZnO is to use nonequilibrium growth techniques, such as molecular doping or epitaxy. It has been recently demonstrated that nitrogen impurities can be activated into acceptor states using pulse thermal processing.⁸ The codoping method⁹ which uses acceptors and donors simultaneously (acceptor-donor-acceptor and donor-acceptor-donor complexes to achieve *p*- and *n*-type conductivities, respectively) could be another approach to improve and control conductivity. It has been proposed that applying this concept for GaN and AlN increases the solubility of the dopants, increases the activation rate by decreasing the ionization energy of acceptors and donors, and increases the mobility of the carriers. In order to decrease the ionization energy of the N acceptor in ZnO, Yan *et al.*¹⁰ proposed a concept of codoping which uses one donor (Ga) and one acceptor (N) to form a passive complex (Ga-N), which creates fully occupied impurity bands above the valence-band maximum (VBM). With further doping, N acceptors will bind to the complex (Ga-N) and effectively dope the fully occupied impurity bands, thus decreasing the ionization energy of the acceptor. Wang and Zunger¹¹ suggested a “cluster-doping” approach for ZnO and found that clusters of (Ga-3N) and (Ga-4N) create both good solubility and local stability for *p*-type ZnO with an NO source for nitrogen, as well as shallower defect levels, which will increase the ionizability. There have been several experimental groups

reporting *p*-type ZnO grown by the codoping approach. Reports include (Al,N) codoping by dc reactive and rf magnetron sputtering,^{12,13} (Ga,N) codoping by metal-organic chemical vapor deposition,¹⁴ pulsed laser deposition,¹⁵ and rf magnetron sputtering;^{13,16} and (In,N) codoping by ultrasonic spray pyrolysis.¹⁷ Very recently, Wang *et al.*¹⁴ reported that the N/Ga ratio in the doping process has a critical influence on the chemical bonding of nitrogen in ZnO:(N,Ga) films. They have shown evidence of the formation of the desired dopant species GaN₂, GaN₃, and GaN₄ from x-ray photoelectron spectra and found effective *p*-type doping. A recent experiment comparing (Al,N) codoping and (Ga,N) codoping showed that the N concentration in ZnO is greatly enhanced by (Ga,N) codoping.¹³ So far, Ga and N codoping has produced the best codoped *p*-type ZnO.^{6,13,15} To date, there are no detailed first-principles studies comparing the behaviors of (Al,N) and (Ga,N) codoping in ZnO.

Using density-functional theory (DFT), we investigate the atomic structure and electronic properties of monodoping of Al, Ga, and N, and codoping or cluster doping of (Al,N) and (Ga,N) in ZnO. We find that substitutional incorporation of both Al and Ga on the Zn site acts as donors that have a tendency to form passive complexes with N atoms located on nearest-neighbor oxygen sites. The (Al-N) and (Ga-N) complexes induce fully occupied defect states above the VBM of ZnO. Doping further N atoms results in (Al-2N) or (Ga-2N) complexes, which act as acceptors with a significantly smaller ionization energy compared to isolated N acceptors in ZnO. We compare the interactions between (Al-N) pairs, (Ga-N) pairs, the interactions between the (Al-N) complex and a substitutional nitrogen atom on the oxygen site, and the (Ga-N) complex and a substitutional nitrogen atom. Our results indicate that the (Ga,N) codoping system is better for obtaining *p*-type ZnO, which supports and helps explain recent experimental results.^{13,14}

II. CALCULATION METHOD

All the calculations are performed using DFT and the generalized gradient approximation (GGA) of Perdew *et al.*¹⁸ for the exchange-correlation functional as implemented in the *ab initio* ESPRESSO code.¹⁹ Ultrasoft pseudopotentials¹⁹ which include the Zn 3*d* states in the valence shell and scalar-relativistic corrections are used. The wave functions are expanded in plane waves with an energy cutoff of 60 Ry. We use 96-atom wurtzite (*wz*) supercells where all the atomic positions are fully relaxed. A reciprocal space **k**-point mesh of 3 × 3 × 3 is employed.

The formation energy of a defect in a given charge state *q* can be expressed as

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

where $E_{\text{tot}}[\text{D}^q]$ is the total energy of the supercell containing the defect and $E_{\text{tot}}[\text{ZnO}]$ is the total energy of the equivalent supercell containing only bulk ZnO. n_i and μ_i are the number and the chemical potential of the atoms added to (positive

n_i), or taken from (negative n_i), the bulk reference supercell in order to create the defect, respectively. E_F is the Fermi level, referenced to the valence-band maximum. E_v is the bulk VBM and ΔV is a correction term, which can be obtained by aligning the reference potential in the defect supercell with that in the bulk (see Ref. 20 for details). The atom chemical potentials μ_i depend on the experimental conditions under which the material is grown. For zinc-rich conditions, $\mu_{\text{Zn}} = E_{\text{Zn}}$ (bulk), and for oxygen-rich conditions, $\mu_{\text{O}} = 1/2 E_{\text{O}_2}$, where E_{Zn} (bulk) and E_{O_2} are the total energies of a Zn atom in bulk Zn and of the oxygen molecule, respectively. The chemical potential for oxygen (zinc) under Zn-rich (O-rich) conditions can be determined from the assumption of thermal equilibrium: $\mu_{\text{Zn}} + \mu_{\text{O}} = \mu_{\text{ZnO}}$, where μ_{ZnO} is the chemical potential of ZnO, which can be taken as E_{ZnO} (bulk), the total energy of a bulk ZnO stoichiometric unit. We present our results under Zn-rich conditions, for which experiments^{7,15} were performed. Zn-rich conditions were suggested to increase the N solubility.²¹ For the case of an impurity or a dopant, the chemical potential of these species will also appear. In the present work we consider defects involving N, Al, and Ga atoms. We consider two gas sources for nitrogen: N₂ and NO. For an N₂ source, we set $\mu_{\text{N}} = 1/2 \mu_{\text{N}_2}$ and $\mu_{\text{N}} = \mu_{\text{NO}} - \mu_{\text{O}}$ for an NO source. To avoid formation of competing secondary phases, i.e., bulk Al and Ga and compounds Al₂O₃, AlN, Ga₂O₃, and GaN, we require $\mu_{\text{M}} \leq E_{\text{M}}$ (bulk), $2\mu_{\text{M}} + 3\mu_{\text{O}} \leq \Delta H_f(\text{M}_2\text{O}_3)$, and $\mu_{\text{M}} + \mu_{\text{N}} \leq \Delta H_f(\text{MN})$, where $M = (\text{Ga}, \text{Al})$. By comparing the chemical potential of μ_{M} derived from the above upper limits for the two sources of nitrogen, we find that μ_{M} obtained from the bulk metal is the greatest (least stable). Thus, we consider μ_{M} derived from both its nitride and oxide. The experimental heat of formation²² (−0.24 eV) for Zn₃N₂ indicates that this phase is only weakly stable and moreover Zn₃N₂ is not observed experimentally thus we do not consider the possible formation of this phase. The calculated heats of formations for Al₂O₃ and AlN are −15.01 eV/f.u. [experiment: −17.01 eV (Ref. 1) and DFT-GGA: −16.42 eV (Ref. 23)] and −2.84 eV [experiment: −3.29 eV (Ref. 1) and DFT-GGA: −2.70 eV (Ref. 24)], respectively. For Ga₂O₃ and GaN, respectively, the values are −8.60 eV/f.u. (experiment: −11.06 eV)¹ and −0.92 eV [experiment: −1.12 eV (Ref. 1) and DFT-GGA: −0.91 eV (Ref. 24)]. The transition level $\epsilon(q_1/q_2)$ is defined as the Fermi-level position where charge states q_1 and q_2 have equal energy.

To determine whether it is energetically preferred that two dopants bind, e.g., Al_{Zn} and N_O, in the neutral charge state, we calculate the binding energy which is defined as

$$E_b(\text{ZnO:AlN}) = E_{\text{tot}}(\text{ZnO:AlN}) + E_{\text{tot}}(\text{ZnO}) - E_{\text{tot}}(\text{ZnO:N}) - E_{\text{tot}}(\text{ZnO:Al}), \quad (2)$$

where $E_{\text{tot}}(\text{ZnO:AlN})$, $E_{\text{tot}}(\text{ZnO:N})$, and $E_{\text{tot}}(\text{ZnO:Al})$ are the total energies for supercells containing defects Al_{Zn}N_O, N_O, and Al_{Zn}, respectively. A negative value of E_b corresponds to a metastable or a stable bound dopant pair when both are present in the system. Extension of Eq. (2) to other complexes and charged states is straightforward.

III. RESULTS

A. Bulk properties

The optimized wz -ZnO lattice constants, using an $8 \times 8 \times 8$ \mathbf{k} -point mesh and an energy cutoff of 60 Ry are $a = 3.295$ Å, $c/a = 1.611$, and $u = 0.379$, which compare well with the experimental values¹ (3.25 Å, 1.602, and 0.378). The same energy cutoff of 60 Ry is used for all the calculations in this paper. Furthermore, for all the bulk systems (described later) an $8 \times 8 \times 8$ \mathbf{k} -point mesh is also used. The heat of formation ΔH_f is obtained as the difference between the total energy of the bulk ZnO (per cation-anion pair), the total energy of a bulk Zn atom and half that of the oxygen molecule, i.e., $\Delta H_f = E_{\text{tot}}^{\text{ZnO}} - E_{\text{tot}}^{\text{Zn}} - 1/2 E_{\text{tot}}^{\text{O}_2}$, and is calculated to be -2.85 eV. This value is consistent with that from a previous DFT-GGA study²⁵ where the value was -2.93 eV. The reported experimental value¹ is -3.56 eV; thus, the calculated values underestimate the experimental result. Compared to the experimental band gap¹ of 3.20 eV, the calculated band gap of 0.72 eV is underestimated, but this is consistent with other DFT-LDA or DFT-GGA studies^{3,25-28} which give values in the range of 0.7–0.9 eV.

We perform spin-unrestricted calculations to study the oxygen atom and molecule. A cubic supercell with the length of 20 bohr is used for the calculation of both the oxygen atom and the oxygen molecule. The bond length and the binding energy of O_2 are calculated to be 1.23 Å and 3.25 eV per atom, exhibiting the well-known overbinding. Our results are consistent with other theoretical values.^{29,30} From experiment, the corresponding values are 1.21 Å and 2.53 eV per atom.¹ For bulk Zn in the hexagonal structure, the cohesive energy is calculated to be -1.09 eV with optimized lattice constants of $a = 2.671$ Å and $c/a = 1.844$. The experimental cohesive energy³¹ is -1.35 eV and the lattice constants¹ are $a = 2.665$ Å and $c/a = 1.856$.

For bulk Al, we obtained an optimized lattice constant of $a = 4.03$ Å and a cohesive energy of -3.64 eV, which are in good agreement with other DFT-GGA calculations.^{24,32} The experimental values³¹ are $a = 4.05$ Å and $E_c = -3.39$ eV. For bulk α -Ga, the calculated lattice constants are $a = 4.625$ Å, $b = 7.75$ Å, and $c = 4.51$ Å. These values are close to those obtained from other DFT-GGA calculations²⁴ with $a = 4.59$ Å, $b = 7.76$ Å, and $c = 4.56$ Å and experimental values of $a = 4.52$ Å, $b = 7.66$ Å, and $c = 4.53$ Å.¹ The calculated cohesive energy is -2.71 eV, which is close to the experimental value³¹ of -2.81 eV. The calculated binding energy of the nitrogen molecule is 4.96 eV per atom, taking into account the spin-polarization energy (3.22 eV) for the nitrogen atom. The bond length of N_2 is found to be 1.11 Å. Our results compare well with other *ab initio* (DFT-GGA) calculations.^{32,33} The corresponding experimental values are 4.90 eV per atom and 1.10 Å.¹

B. Single dopants

We first consider the single N, Al, and Ga dopants in wz -ZnO. For substitutional N on the O site, N_{O} , in the neutral charge state, we find that the “apical” Zn atom moves inward by 2.34% and the three equivalent “planar” Zn atoms relax

inward by 2.83%. N_{O} acts as a single acceptor, inducing a defect state with a hole at the top of the valence band. The calculated ionization energy of the N acceptor is 0.33 eV, which is in good agreement with other theoretical calculations, where the predicted value is about 0.3–0.4 eV above the VBM.^{3,5,11,28} Rather similar to the neutral charge state, N_{O}^- induces an inward displacement of the apical N atom and three planar N atoms of 3.29% and 3.98%, respectively.

Substitutional Al on a Zn site, Al_{Zn} , creates a singly occupied singlet defect state in the conduction band and thus acts as a donor in ZnO. In the 1+ charge state, the apical and the planar distances between Al and O atoms are 9.6% and 10.0% shorter than the values in bulk ZnO, respectively. The large contraction can be understood in that the calculated heat of formation per oxygen atom of Al_2O_3 is greater (-5.0 eV) than that of ZnO (-2.85 eV), indicating a stronger Al-O bond.

Substitution of Ga on a Zn site, Ga_{Zn} , also acts as a donor in ZnO and creates a singly occupied singlet defect state in the conduction band. The apical and the planar distances between the Ga and O atoms are 5.0% and 5.6% shorter than the values in bulk ZnO, respectively.

In Fig. 5 the formation energies of those single dopants (along with those of the complexes, discussed later) are shown as a function of the Fermi level E_F under Zn-rich conditions for [(a) and (b)] an N_2 source and for [(c) and (d)] an NO source. The slopes correspond to the charge state and the kinks correspond to the transition levels. The formation energies of N_{O} in the neutral state are 1.58 and -2.24 eV with N_2 and NO sources, respectively. The high value of the former indicates that the N-doped ZnO system using an N_2 source may not readily to produce p -type conductivity, which is consistent with experimental results³⁴ and a previous DFT investigation.¹¹ The very low value of the formation energy of N_{O} when using an NO source, on the other hand, suggests good incorporation of nitrogen. Interestingly, recent experiments find this and in addition that it leads to p -type conductivity; however, this is only metastable and, with time, it converts to n -type.³⁴ This phenomenon was explained on the basis of DFT calculations which showed that N_{O} may attract another N atom leading to N_2 on an O site, which is a donor, or that N_{O} may diffuse away, leaving a nitrogen vacancy, which is also a donor. With regard to the Al and the Ga donors, the formation energies are very high [see Fig. 5(c)] using an NO source and the chemical potential of Al/Ga obtained from AlN/GaN. Under other experimental conditions considered [see Figs. 2(b), 2(d), and 5(a)], both Al and Ga donors have lower formation energies, thus contributing to the n -type conductivity. Experimentally, high-quality n -type ZnO has been achieved by doping with the group-III elements such as Al, Ga, and In.³⁵

C. Codoping with (Al,N)

To investigate the possibility of achieving p -type ZnO using Al and N codoping, we follow the approach of a previous study of codoping (Ga_2N) proposed by Yan *et al.*¹⁰ We investigate the interaction between Al_{Zn} and N_{O} and find, out of the configurations tested, that they prefer to be located

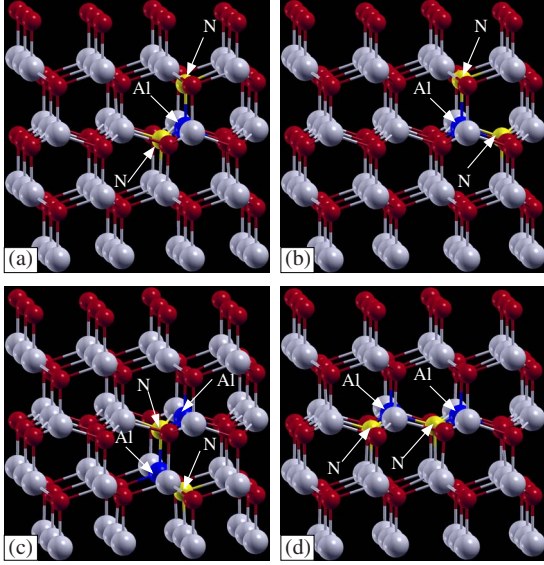


FIG. 1. (Color online) Atomic geometry of the relaxed structures in ZnO of the (a) (Al-2N)-B, (b) (Al-2N)-A configurations, (c) the armchair 2(AIN), and (d) the zigzag 2(AIN) configurations in the neutral charge state. The light gray and dark gray (red) spheres represent Zn and O atoms, respectively. The Al (large gray/blue) and N (small gray/yellow) atoms are indicated by the arrows.

on nearest-neighbor sites in the same (0001) plane. This configuration is referred to as (Al-N)-A, and the binding energy is -1.30 eV, relative to the single defects Al_{Zn} and N_{O} , while the binding energy is -0.22 eV referenced to Al_{Zn}^+ and N_{O}^- . The energy of the structure with Al_{Zn} and N_{O} on the nearest-neighbor sites along the c -axis is about 0.05 eV higher, and the energy of the configuration with Al_{Zn} and N_{O}

“far apart” (~ 9 Å) is 0.27 eV higher. As discussed above, Al_{Zn} is a donor and N_{O} is an acceptor; on forming the (Al-N) complex, we find that there are no longer any states in the band gap, except two fully occupied singlet states above the VBM [see Fig. 2(a)]. We denote the top of the fully occupied defect states as the “new VBM.” We confirm that these states are related to the Al-N complex by plotting the spatial distribution of the single particle wave functions at the Γ point. The wave functions also exhibit a notable coupling to the bulk oxygen atoms of the host. The distance between Al and N in the complex (Al-N)-A is 1.84 Å, and the bond length of Al and its nearest-neighbor O atoms is 1.83 Å on average, which is 8.8% shorter than the average bond length (2.01 Å) of Zn-O in bulk ZnO.

For two pairs of (Al-N)-A, denoted as 2(AIN), we consider the pairs in “armchair” [along the c axis, shown in Fig. 1(c)] and “zigzag” [perpendicular to the c axis, shown in Fig. 1(d)] configurations and a configuration with the pairs far apart (~ 8 Å). There is only a very small energy difference of 0.01 eV between the armchair and the far apart configurations, with the far apart configuration being slightly more favorable. The energy of the zigzag configuration is 0.03 eV higher than the far apart configuration. The calculated binding energies, with respect to two isolated (Al-N)-A complexes, are listed in Table I. These results indicate that the interaction between (Al-N) pairs is very weak.

When a second N atom is added to a nearest-neighbor site of the configuration [(Al-N)-A], there are two possible locations: one in the same plane and one along the c axis. We consider both of them as well as an additional configuration proposed by experiment¹² [(Al-2N)-B, shown in Fig. 1(a)] with the additional N atom located at a next-nearest-neighbor site. We find the total energies of the configurations with the N atom located at the nearest-neighbor sites are almost de-

TABLE I. Binding energies E_b (in eV) of defect complexes in ZnO. A negative value indicates a bound complex. The binding energies of the defects are computed with respect to the defect combinations in the parentheses. “ac” and “zz” indicate the armchair and zigzag configurations, respectively, and “far” indicates the configuration with far apart defect pairs (see text). Note, for simplicity, for complexes we did not use a subscript to indicate that the N atoms occupy O sites and (Al,Ga) occupy Zn sites.

Defect	E_b	Defect	E_b		
Al-N	-1.30	(Al _{Zn} +N _O)	Ga-N	-1.55	(Ga _{Zn} +N _O)
Al-N	-0.22	(Al _{Zn}^++N_{O}^-)}}	Ga-N	-0.43	(Ga _{Zn}^++N_{O}^-)}}
Al-2N	-0.006	(Al-N+N _O)	Ga-2N	-0.21	(Ga-N+N _O)
(Al-2N) ⁻	-0.03	(Al-N+N _{O}^-)}	(Ga-2N) ⁻	-0.24	(Ga-N+N _{O}^-)}
Al-3N	0.03	(Al-2N+N _O)	Ga-3N	-0.17	(Ga-2N+N _O)
(Al-3N) ⁻	0.02	[(Al-2N) ⁻ +N _O]	(Ga-3N) ⁻	-0.24	[(Ga-2N) ⁻ +N _O]
(Al-3N) ²⁻	-0.05	[(Al-2N) ⁻ +N _{O}^-]}	(Ga-3N) ²⁻	-0.13	[(Ga-2N) ⁻ +N _{O}^-]}
Al-4N	0.05	(Al-3N+N _O)	Ga-4N	-0.18	(Ga-3N+N _O)
(Al-4N) ⁻	0.07	[(Al-3N) ⁻ +N _O]	(Ga-4N) ⁻	-0.20	[(Ga-3N) ⁻ +N _O]
(Al-4N) ⁻	-0.01	[(Al-3N)+N _{O}^-]}	(Ga-4N) ⁻	-0.30	[(Ga-3N)+N _{O}^-]}
(Al-4N) ²⁻	0.01	[(Al-3N) ²⁻ +N _O]	(Ga-4N) ²⁻	-0.27	[(Ga-3N) ²⁻ +N _O]
(Al-4N) ³⁻	0.05	[(Al-3N) ²⁻ +N _{O}^-]}	(Ga-4N) ³⁻	0.03	[(Ga-3N) ²⁻ +N _{O}^-]}
2(AIN)-zz	0.007	(Al-N+Al-N)	2(GaN)-zz	-0.20	(Ga-N+Ga-N)
2(AIN)-ac	-0.006	(Al-N+Al-N)	2(GaN)-ac	-0.18	(Ga-N+Ga-N)
2(AIN)-far	-0.01	(Al-N+Al-N)	2(GaN)-far	-0.01	(Ga-N+Ga-N)

TABLE II. Calculated transition energy levels ϵ (in eV) for the defect complexes in ZnO.

Defect	ϵ (0/1-)	ϵ (1-/2-)	ϵ (2-/3-)
N _O	0.33		
Al-2N	0.17		
Al-3N	0.15	0.18	
Ga-2N	0.14		
Ga-3N	0.07	0.29	
Ga-4N	0.05	0.22	0.46

generate, while the energy of configuration B is about 0.039 eV higher. The energy of the configuration with the additional N atom far apart (~ 8 Å) from the (Al-N)-A complex is 0.044 eV higher. Thus, the second N atom slightly prefers to occupy nearest-neighbor sites of Al as in the complex (Al-2N)-A shown in Fig. 1(b). The binding energy of (Al-2N)-A is extremely weak, namely, -0.006 eV with respect to the (Al-N)-A complex and an isolated N atom (in the neutral state), and the binding energy of this complex in the 1- charge state is -0.03 eV relative to the neutral (Al-N)-A complex and a N atom in the 1- charge state. The neutral (Al-2N)-A complex yields a singlet defect state with a hole above the new VBM (which is above the VBM of bulk ZnO), hence acting as an acceptor. The distance between Al and the N atoms is 1.87 Å both along the *c* axis and in plane. The bond length of Al-O is 1.84 Å on average, and the average distance between N and Zn atoms is 1.98 Å. The calculated ionization energy of the (Al-2N)-A complex is 0.17 eV, shallower than the single N acceptor.

We also consider a higher nitrogen concentration complex, (Al-3N), by putting the additional N atom on the nearest-neighbor oxygen site of the (Al-2N)-A complex. The binding energy relative to the (Al-2N)-A complex and the single N atom (in their neutral states) is 0.03 eV, which indicates that the neutral complex (Al-2N)-A does not like to bind with an additional nitrogen atom. In the 2- charge state, the binding energy is -0.05 eV relative to the (Al-2N)-A complex and the N atom in their 1- charge states, indicating a mutually attractive weak interaction between the activated defects. The (Al-3N) complex has a (0/1-) transition energy at 0.15 eV and a (1-/2-) transition at 0.18 eV above the new VBM (as listed in Table II). In the 2- charge state, the average distance between Al and N atoms is 1.87 Å (close to the average Al-N bond length of 1.89 Å in *wz*-AlN), and the average bond length of N-Zn is 1.96 Å.

We further increase the nitrogen concentration with an additional N atom on the nearest-neighbor oxygen site of the (Al-3N) complex to check if this configuration may have a larger binding energy than the (Al-2N) and the (Al-3N) cases. We find that the binding energy of the (Al-4N) complex is 0.05 eV referenced to the neutral (Al-3N) complex and neutral N_O; thus, it is unstable. This complex induces two singlet defect states above the new VBM with three holes; thus, it would act as a triple acceptor if it would be stable. The binding energies in the different charge states, with respect to the (Al-3N) complex in the various charge states and N_O in the neutral or 1- charge state are listed in

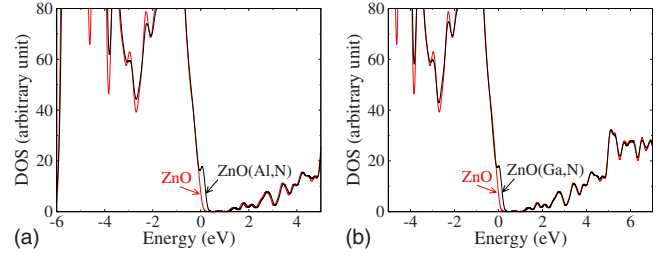


FIG. 2. (Color online) Calculated density of states for bulk ZnO shown as the thin (red) curves and for supercells containing (a) an (Al-N)-A complex and (b) a (Ga-N)-A complex, shown as the thick (black) curves as indicated.

Table I. The results show that the interaction between the (Al-3N) complex and a N dopant is weak and largely unstable.

In Fig. 5 the formation energy of the (Al-*m*N) (*m*=1,4) complexes are shown. It can be seen that the (Al-2N) acceptor has a very similar formation energy to the isolated N acceptor, with the exception of an NO source and the Al solubility being limited by Al₂O₃ formation [Fig. 5(d)]; here the formation energy is notably lower. The formation energies of the (Al-3N) and (Al-4N) complexes are higher than the (Al-2N) complex for an N₂ source, indicating that *p*-type cluster doping is not expected to be successful under these conditions. The notably lower formation energies of the (Al-3N) and (Al-4N) complexes with the NO source indicate that such complexes could promote *p*-type conductivity if their binding energies would be greater. However, as described above, on the basis of the very weak and/or unstable binding energies, such complexes are unlikely to form.

D. Codoping with (Ga,N)

Similarly to our investigation of (Al,N) codoped ZnO, for codoping (Ga,N) in ZnO, we consider the geometry with Ga and N located at nearest-neighbor sites in the same (0001) plane and along the *c* axis and find that the former configuration is energetically more favorable than the latter with the energy difference of 0.03 eV. We therefore focus on the more stable configuration of the (Ga-N) complex, denoted as (Ga-N)-A, for further calculations. The binding energy of this complex is -1.55 eV relative to the single (neutral) dopants Ga_{Zn}⁺ and N_O⁻. With respect to Ga_{Zn}⁺ and N_O⁻, the binding energy is -0.43 eV. As for codoping with (Al,N), the (Ga-N) complex introduces two fully occupied singlet impurity bands above the VBM (represented as the new VBM) as shown in Figs. 2(b) and 3(a). The single particle wave functions are also plotted at the Γ point for eigenvalues close to the new VBM, where coupling can be seen between the defect state and O-related bulk states, indicating a delocalized nature of the defect states. The Ga-N bond length is 1.87 Å, which is 7.1% shorter than the corresponding bond length (2.01 Å) of Zn-O in bulk ZnO. The average bond lengths of Ga-O and N-Zn are 1.94 and 1.97 Å, respectively, which are 3.5% and 2.0% shorter than the average Zn-O bond length in the bulk. We also consider two pairs of (Ga-N), denoted as 2(Ga-N), in both armchair and zigzag configurations, and a

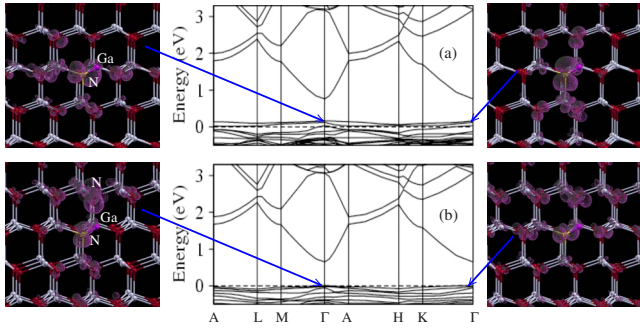


FIG. 3. (Color online) Band structures for the (a) (Ga-N)-A and (b) (Ga-2N)-A complexes in the neutral charge state in ZnO. The horizontal dotted line in the upper band structure (a) represents the position of the VBM of bulk ZnO; in the lower band structure (b) it represents the Fermi level of the defect complex system. Isosurface plots are shown of the charge density induced by the defect states as indicated by the arrows. The $0.002e/\text{bohr}^3$ isovalues are shown. Light gray and dark gray (red) spheres indicate Zn and O atoms, respectively. The Ga (dark gray/purple) and N (gray/yellow) atoms are indicated.

configuration with the pairs far apart (~ 8 Å) as well. The zigzag configuration is slightly more favorable than the arm-chair configuration, with an energy difference of only 0.01 eV. The energy of the far apart configuration is about 0.20 eV higher than the zigzag configuration. The binding energies for these (Ga-N) pairs, as listed in Table I, are calculated with respect to two separated (Ga-N) complexes. Our results indicate that the GaN pairs prefer to stay together in ZnO, which means that the concentration of the defects creating the impurity band is likely to be tunable up to a high value.

For the complex with one Ga and two N atoms, we consider the configuration (Ga-2N)-A, with both N atoms, one in the same plane and one along with the c axis, occupying the nearest-neighbor O sites of the Ga atom. Previous calculations suggested that this structure is energetically favorable.²¹ The energy of the configuration with the second N atom far apart (~ 8 Å) from the (Ga-N) complex is 0.21 eV higher. The binding energy of the (Ga-2N)-A complex is -0.21 eV, with respect to $\text{Ga}_{\text{Zn}}\text{N}_{\text{O}}$ and N_{O} in the neutral charge state, while the value of the binding energy is -0.24 eV when calculated in the single negative charge state and referenced to $\text{Ga}_{\text{Zn}}\text{N}_{\text{O}}$ and N_{O}^- . These values are notably greater than those of the corresponding (Al,N) complexes. The (Ga-2N)-A complex acts as an acceptor with a hole in a singlet defect state above the new VBM [as shown in Fig. 3(b)] and an ionization energy of 0.14 eV, in good agreement with a previously calculated value of 0.1 eV,¹⁰ and a measured activation energy of less than 0.15 eV.^{36,37} In the neutral charge state, the average distance between Ga and N is 1.91 Å, and the average bond lengths of Ga-O and N-Zn are 1.96 and 1.98 Å, respectively. In the 1- charge state, the average bond length of Ga-N is 1.90 Å, the average distance between Ga and O is increased slightly to 1.98 Å, and the average distance between N and Zn is decreased slightly to 1.96 Å.

When another nearest-neighbor nitrogen atom in the same plane is added to the (Ga-2N)-A complex, the resulting bind-

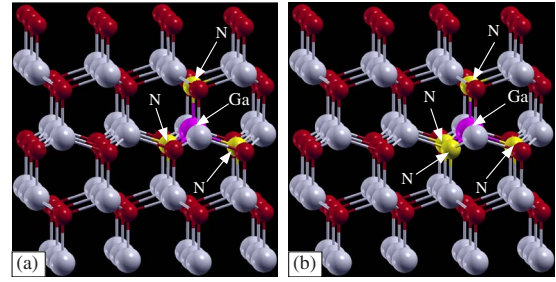


FIG. 4. (Color online) Atomic geometry of the relaxed structures in ZnO of (a) the (Ga-3N) and (b) the (Ga-4N) complexes in the neutral charge state. Light gray and dark gray (red) spheres indicate Zn and O atoms, respectively. The Ga (large dark gray/purple) and N (small gray/yellow) atoms are indicated by the arrows.

ing energy in the neutral charge state is -0.17 eV [referenced to the (Ga-2N)-A complex and N_{O}] and is -0.13 eV in the 2- charge state with respect to the (Ga-2N)-A complex in the 1- charge state and N_{O}^- . This indicates that the complex (Ga-3N) is favorable with respect to the (Ga-2N)-A complex and an isolated N dopant. This (Ga-3N) complex [see Fig. 4(a)] induces a singlet defect state with two holes above the new VBM, thus acting as a double acceptor. The transition level from the neutral to the 1- charge state is 0.07 eV and from 1- to 2- it is 0.29 eV above the new VBM. In the neutral charge state, the average Ga-N bond length is 1.93 Å, the average distance between Ga and O atoms is 1.98 Å, and the average bond length of Zn-N is 1.98 Å. In the 2- charge state, the average Ga-N bond length is 1.92 Å, the average distance between Ga and O atoms is 2.03 Å, and the average distance between N and Zn atoms is 1.95 Å.

We also consider the interaction between the (Ga-3N) complex and a N atom located at the fourth nearest-neighbor O site of the Ga atom and find that the binding energy of the complex (Ga-4N) is -0.18 eV, relative to neutral (Ga-3N) and N_{O} . The (Ga-4N) complex acts as a triple acceptor with three holes located at two singlet defect states above the new VBM and with a (0/1-) transition at 0.05 eV, a (1-/2-) transition at 0.22 eV, and a (2-/3-) transition at 0.46 eV. The binding energies of this complex in the different charge states, as listed in Table I, are referenced to the (Ga-3N) complex in the stable charge states and N_{O} in the neutral and the 1- charge states. The negative values of the binding energies indicate that the (Ga-3N) complex is attractive to an isolated N acceptor, while, in the 3- charge state, there is a weakly repulsive interaction between the (Ga-3N) complex in the 2- charge state and N_{O}^- . The atomic structure of this defect complex in the neutral charge state is shown in Fig. 4(b). In the neutral charge states, the average Ga-N bond length is 1.95 Å (close to the average Ga-N bond length of 1.97 Å in wz -GaN); only minor differences occur between different negative charge states.

In Fig. 5 the formation energies of the various (Ga,N) complexes are shown. It can be seen that independent of the experimental conditions, the (Ga-2N) acceptor has a lower or very similar formation energy, and a lower transition level, compared to the isolated N acceptor, thus improving the prospect of p -type doping. Similarly to the (Al,N) codoping

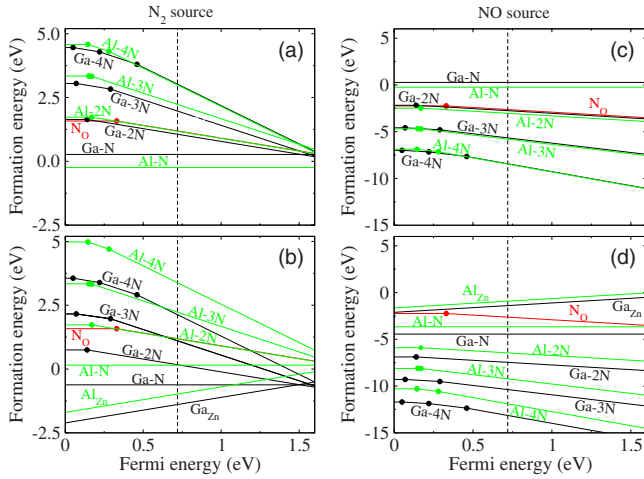


FIG. 5. (Color online) Formation energies as a function of the Fermi level for defects and complexes in wurtzite ZnO under Zn-rich conditions: for an N_2 source [left panels (a) and (b)] and for an NO source [right panels (c) and (d)] of nitrogen. In (a) and (c), μ_{Al} and μ_{Ga} are derived from equilibrium with AlN and GaN, respectively. In (b) and (d), μ_{Al} and μ_{Ga} are determined by equilibrium with Al_2O_3 and Ga_2O_3 , respectively. The vertical dashed lines represent the calculated band gap of bulk ZnO. The kinks correspond to the transition levels (denoted by solid dots).

or cluster doping system, for an N_2 source, the formation energies of the (Ga,N) complexes are high, thus indicating that achieving p -type conductivity would not be expected. For the NO source, the formation energies and the transition levels of the (Ga-3N) and (Ga-4N) complexes are lower than the (Ga-2N) complex, which indicate that cluster formation helps to create both local stability of nitrogen and good solubility for p -type doping of ZnO.

IV. DISCUSSION

Figure 2 shows the calculated total density of states for the bulk ZnO host (thin red curve) and a supercell containing a complex of (a) (Al-N) and (b) (Ga-N) (thick black curves). It is clear that the formation of a passive (Al-N) or (Ga-N) complex does not change the basic electronic structure but generates additional fully occupied defect bands above the VBM. These defect states can be regarded as forming a new VBM, which would be suitable for increasing the hole concentration provided that the states are sufficiently delocalized. For codoping of ZnO with GaN, a high concentration of (Ga,N) complexes will be likely due to the found attractive interaction between them. This, together with the identified hybridization of the related (GaN) induced states with host states at the top of the ZnO VBM, will likely assure that these defect states will be extended throughout the system. When excess N atoms are available, they will dope the passivated system. The transition will occur between the N defect levels and the new VBM, rather than the original valence band of the pure ZnO. Thus, both (Al-2N) and (Ga-2N) codoping complexes have shallow acceptor levels compared to the single N dopant and thus nitrogen in the (Al-2N) and (Ga-2N) complexes will be more easily ionized than isolated

N. There are some experimental verifications of these codoping systems,^{12,13,15} but a potential problem is that isolated Al or Ga atoms (if there is excess Al or Ga in the system) will compensate the (Al-2N) or (Ga-2N) acceptors,³⁸ thus possibly preventing the achievement of p -type conductivity.^{39,40}

Based on the present study, the weak interactions between two (Al-N) complexes and between the (Al-2N) complex and a N atom (on a neighboring oxygen site) indicate that the N concentration cannot be significantly increased by Al and N codoping or cluster doping. In contrast, two (Ga-N) complexes prefer to bind together in the same (0001) plane, and the (Ga-2N) complex has a tendency to form clusters of (Ga-3N) and (Ga-4N) with N atoms on the nearest-neighbor O sites. The transition levels (0/1-) and (1-/2-) of (Ga-3N) and (Ga-4N) complexes are smaller than the isolated nitrogen acceptor. Both these factors will further enhance the solubility and the activation of N acceptors.

There are two possible explanations for the ability of the Ga dopant to bind more nitrogen atoms than the Al dopant. First, compared to the ionic radius of Al (0.535 Å), the ionic radius of Ga (0.62 Å) is closer to that of Zn (0.74 Å). Thus the single Ga dopant induces a smaller lattice distortion when being incorporated on a Zn site, and thus a smaller energy cost. Furthermore, the calculated lattice constants of ZnO are $a=3.295$ Å, $c/a=1.611$, and $u=0.379$, while those of AlN are $a=3.124$ Å, $c/a=1.597$, and $u=0.377$, and of GaN are $a=3.214$ Å, $c/a=1.632$, and $u=0.382$. Thus, the lattice mismatch (2.2%) between wz -GaN and wz -ZnO is smaller than the lattice mismatch (5.0%) between wz -AlN and wz -ZnO. A second explanation is based on the calculated heats of formation of the respective Ga and Al oxides and nitrides. Our calculated heat of formation for Al_2O_3 is -15.01 eV/formula unit, or -3.0 eV per atom compared to -2.84 eV for AlN per formula unit, or -1.42 eV per atom (reduction by 1.58 eV); while for Ga we have the formation energy of -8.60 eV/formula unit or -1.72 eV per atom, and for GaN, -0.92 eV/formula unit or 0.46 eV per atom (reduction by 1.26 eV). This indicates qualitatively that a doped Al atom in ZnO (with O neighbors) would experience a greater loss in binding energy when bonded to N neighbors (substituting the O neighbors) as compared to the case for a doped Ga atom.

For the N_2 source [see Figs. 5(a) and 5(b)], the single acceptor (Ga-2N) is slightly [Fig. 5(a)] or more [Fig. 5(b)] favorable and has a lower acceptor ionization energy, compared to the (Al-2N) complex and the single nitrogen acceptor, whereas the high formation energies of the (Ga-3N), the (Ga-4N), the (Al-3N), and the (Al-4N) complexes imply a limited N solubility. Using the NO source, if the Al and the Ga solubilities are limited by AlN and GaN as shown in Fig. 5(c), respectively, the formation energies of (Ga-3N) and (Ga-4N) complexes are lower than (Ga-2N) and (Al-2N) complexes and similar to those of the unstable (Al-3N) and (Al-4N) complexes. Thus, compared to (Al,N) codoping or cluster doping system, the (Ga,N)-related cluster formation would create good p -type conductivity. For (Ga,N) codoping, our results in Figs. 5(a) and 5(c) are consistent with the previous DFT-GGA calculations.¹¹ When the chemical potentials of Al and Ga are determined by equilibrium of Al_2O_3 and Ga_2O_3 , respectively, the formation energies [Fig. 5(d)] of

the (Ga-2N) acceptor is ~ 4.5 eV lower than that of the N acceptor and ~ 1 eV lower than that of the (Al-2N) acceptor. The formation energies of the (Ga-3N) and the (Ga-4N) complexes are lower than that of the (Ga-2N) and the (Al-3N) complexes over the whole range of the Fermi energy considered. Thus, the lower formation energies, greater binding energies, and lower ionization levels indicate that (Ga,N) codoping or cluster doping is more suitable for achieving *p*-type ZnO compared to that of (Al,N). It has been suggested on the basis of first-principles calculations¹¹ that cluster doping by Ga+4N (i.e., Ga-4N in our notation) is more soluble than codoping ZnO by Ga+2N (i.e., Ga-2N). There is indeed experimental evidence¹⁴ for the formation of (Ga-2N), (Ga-3N), and (Ga-4N) from x-ray photoelectron spectroscopy, which is also consistent with our findings.

V. CONCLUSION

We have studied the electronic and the structural properties of ZnO codoped with aluminum and nitrogen and gallium and nitrogen through first-principles density-functional theory calculations. The isolated substitutional (on the Zn site) Al and Ga act as donors, thus contributing to *n*-type conductivity. N substitution on an O site acts as an acceptor in ZnO and contributes to *p*-type conductivity, with an ionization energy of 0.33 eV. Both Al and Ga bind to N atoms, forming passive (Al-N) and (Ga-N) complexes introducing a fully occupied singlet state above the VBM. These com-

plexes further bind N atoms resulting in single acceptor complexes. Independent of the experimental conditions, the (Al-2N) and the (Ga-2N) acceptors have smaller transition energy levels than the single N acceptor, which indicates that (Al,N) and (Ga,N) codoping could increase the percentage of ionized N dopants. The (Ga-2N) complex can bind additional N atoms on the nearest-neighbor O sites and has a tendency to form clusters of (Ga-3N) and (Ga-4N). For an N₂ source, the higher formation energies of the (Ga,N) and the (Al,N) complexes indicate that *p*-type conductivity would not be expected to be readily achieved. Compared to the (Ga-2N) complex, the cluster (Ga-3N), for an NO source of nitrogen, has a lower formation energy and lower transition levels. The (Ga-4N) complex has the lowest formation energy and the lowest transition levels among the (Ga,N) complexes. In contrast, binding of additional N atoms to the (Al-2N) is either unfavored or only weakly attractive. On the basis of these results, we therefore predict that (Ga,N) codoping of ZnO is likely to yield better *p*-type conductivity than (Al,N) codoping, which is consistent with recent experimental findings.¹³

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