Design of shallow acceptors in ZnO through early transition metals codoped with N acceptors

X. M. Duan, C. Stampfl, M. M. M. Bilek, D. R. McKenzie, and Su-Huai Wei

Design of shallow acceptors in ZnO through early transition metals co-doped with N acceptors

X. M. Duan

Department of Physics, Ningbo University,
Ningbo 315211, P.R. China
and
School of Physics, The University of Sydney, Sydney, New South Wales 2006, Australia

C. Stampfl, M. M. M. Bilek, D. R. McKenzie
School of Physics, The University of Sydney, Sydney, New South Wales 2006, Australia

Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

We perform first-principles density-functional theory calculations to study the atomic and electronic properties of early transition metals (Zr, Ti, Y, and Sc) co-doped with N in wurtzite ZnO. By incorporating early transition metals Ti, Zr, Y and Sc with N into ZnO simultaneously, we find that forming complexes (Zr-2N), (Ti-2N), (Y-N) and (Sc-N) induces fully occupied impurity bands with the N $2p$ character above the valence band maximum of host ZnO. With further doping of N in ZnO, the systems (Zr-2N):N, (Ti-2N):N, (Y-N):N or (Sc-N):N have acceptor ionization energies lower than that of the isolated N acceptor in ZnO. Under different growth conditions (i.e using N_2O or NO source for the nitrogen atoms), we calculate the formation energies of the defect complexes and compare the dopability of the selected co-doped systems. Our results show that the valence band maximum characteristic of ZnO can be altered by compensated donor-acceptor pairs, thus improve the p-type dopability.
PACS numbers: 61.72.Bb 71.55.Cn, 71.55.Gs

PACS numbers:

I. INTRODUCTION

Zinc oxide (ZnO) thin films have prompted great interest as a transparent conductive oxide due to their remarkable electro-optical properties[1]. Both p- and n-type conductivities will be required for development of optically transparent ZnO-based devices, such as light emitting diodes and laser diodes. As grown, ZnO acts as an n-type semiconductor, the origin of which is still under debate; in particular, the energy level of the oxygen vacancy is too deep and the formation energy of the Zn interstitial is too high, so they cannot be the source of n-type conductivity in ZnO[2]. However, it is difficult to achieve p-type conduction in ZnO either due to low dopant solubility or to a high defect ionization energy of the acceptors. To date, considerable effort[3–6] has been made to realize p-type ZnO. It has been suggested, that of the group-V elements, N is the most suitable dopant because it has a high electronegativity and about the same ionic radius as O, and thus should readily substitute on O sites, although theory suggests some difficulty in achieving a shallow acceptor level[7,8]. The solubility of nitrogen dopants in ZnO could be greatly enhanced by non-equilibrium growth techniques, such as epitaxial and molecular doping (NO_2, NO, etc). The traditional co-doping approach[9] by doping donor and acceptor simultaneously is another way to enhance the solubility of a dopant in ZnO. There have been several publications reporting on successful fabrication of codoped p-type ZnO[5,10–16], as well as failures[17–19]. However, the high ionization energy of acceptors, caused by the very low valence band maximum (VBM) of ZnO, is hard to overcome[20]. Recently, Yan *et al*[21], proposed a universal co-doping approach to decrease the ionization of N acceptors, through effective doping of mutually passivated defect pairs (e.g., Ga+N), which creates fully occupied impurity bands above the VBM of ZnO. After the fully compensated insulating phase is formed, excess dopants (here, N) are used to dope the passivated system by ionizing the defect band. Furthermore, the formation of the acceptor-donor pairs also stabilizes the defects. Nevertheless, the calculated acceptor level in this system (0.2 eV) is still too deep to ionize and produce enough holes for device applications operated at room temperature. Therefore, better approaches to create more stable and shallower acceptors in ZnO is still a subject of intense research. One of the reasons that N has a deep level at 0.33 eV above the VBM in ZnO is because N p states couple with neighboring Zn d orbitals, which pushes the N acceptor level up[22]. Replacing Zn by Ga or Al in (Ga+2N) may help a little, because Ga d orbitals are deep and Al d states are high above (unoccupied). We note that d orbitals of the transition metals are above the N p orbitals, so p-d repulsion actually pushes the acceptor level down in energy. Therefore, by co-doping nitrogen with special compensative donors (Zr, Ti, Y and Sc), we anticipate that it can lead to a

semiconducting system with a higher VBM than ZnO. With further doping of N, shallow $(-/0)$ acceptor levels for (Zr-2N):N, (Ti-2N):N, (Y-N):N, (Sc-N):N, and, thus a higher concentration of carriers at working temperature may be expected.

In this paper, we investigate the atomic structure and electronic properties of Zr, Ti, Y and Sc co-doped with N in ZnO through *ab initio* calculations. We find that substitutional Zr or Ti on the Zn site have a strong tendency to form (Zr-2N) or (Ti-2N) complexes with two N atoms located on the nearest neighbor O sites. Substituted Y or Sc exhibits an attractive interaction with a nitrogen atom located on a nearest neighbor site. The (Zr-2N), (Ti-2N), (Y-N) and (Sc-N) complexes induce fully occupied defect states above the VBM of bulk ZnO. With further doping, the systems (Y-N):N and (Sc-N):N have an acceptor ionization energy of 0.14 eV and 0.18 eV, respectively, which is lower than the ionization energy for the isolated N acceptor in ZnO. Doped excess N atoms prefer to occupy the nearest neighbor sites of the Zr and Ti atoms, and the formation of the (Zr-3N), (Ti-3N) and (Ti-4N) nearest neighbor clusters are stable. The (Zr-2N):N and (Ti-2N):N systems have acceptor ionization energies of 0.08 eV and 0.09 eV, respectively. Thus, (Y,N), (Sc,N), (Zr,N) and (Ti,N) co-doping could decrease the acceptor ionization energy and enhance the N dopant solubility in ZnO. Using N_2O and NO gas as the nitrogen source, the solubility of N in ZnO can be further enhanced in the (Zr,N), (Ti,N) and (Ga,N) (from our previous study) co-doped systems. The paper is organized as follows: In Sec. II, we describe the calculation method and Sec. III reports results for single dopants and co-doping. In Sec IV, we discuss the formation energies and transition levels. Sec. V contains the conclusions.

II. CALCULATION METHOD

The calculations are carried out using first-principles density-functional theory (DFT) and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof[23] for the exchange-correlation potential as implemented in the Quantum-ESPRESSO code[24]. The ultrasoft pseudopotentials[24] include the Zn $3d$ 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 (the same energy cutoff is used for all the calculations in this paper). A reciprocal space **k**-point mesh of $3 \times 3 \times 3$ is employed. We use 96-atom wurtzite supercells where all the atomic positions are fully relaxed.

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

$$E^f[\mathrm{D}^q] = E_{\mathrm{tot}}[\mathrm{D}^q] - E_{\mathrm{tot}}[\mathrm{ZnO}] + \sum_i n_i\mu_i + q[E_{\mathrm{F}} + E_v + \Delta V], \tag{1}$$

where $E_{\mathrm{tot}}[\mathrm{D}^q]$ is the total energy of the supercell containing the defect, and $E_{\mathrm{tot}}[\mathrm{ZnO}]$ is the total energy for the equivalent supercell containing only bulk ZnO. n_i and μ_i are the number and chemical potential of the atoms added to ($n_i < 0$), or taken from ($n_i > 0$), 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. [25] for details). The atom chemical potentials, μ_i, depend on the experimental conditions under which the material is grown. For zinc-rich conditions, $\mu_{\mathrm{Zn}} = E_{\mathrm{Zn}}(\mathrm{bulk})$, and for oxygen-rich conditions, $\mu_{\mathrm{O}} = 1/2E_{\mathrm{O}_2}$, where $E_{\mathrm{Zn}}(\mathrm{bulk})$ and E_{O_2} are the total energy of a Zn atom in bulk Zn and the total energy of the oxygen molecule, respectively. The chemical potential for oxygen (zinc) under Zn-rich (oxygen-rich) conditions can be determined from the assumption of thermal equilibrium: $\mu_{\mathrm{Zn}} + \mu_{\mathrm{O}} = \mu_{\mathrm{ZnO}}$, where μ_{ZnO} is the chemical potential of ZnO, which can be taken as $E_{\mathrm{ZnO}}(\mathrm{bulk})$, the total energy of a bulk ZnO stoichiometric unit. The transition level $\epsilon(q_1/q_2)$ is defined as the Fermi-level position where charge state q_1 and q_2 have equal energy.

We present our results under Zn-rich conditions, under which experiments of N-doped[26] and (Ga,N) co-doped[10] p-type ZnO were performed, and where Zn-rich conditions were suggested to enhance the N solubility[27]. For the case of an impurity or a dopant, the chemical potential of these species will also appear. In the present work we consider defect formation energies involving N, Zr and Ti atoms. Experimental work[28] reported the co-doping of Zr and N are performed with an N_2O source. Therefore we use N_2O to determine the nitrogen atom chemical potential and also consider as well an NO source. For an N_2O source, we set the N chemical potential as $\mu_{\mathrm{N}} = 1/2(\mu_{\mathrm{N}_2\mathrm{O}} - \mu_{\mathrm{O}})$, and for an NO source, $\mu_{\mathrm{N}} = \mu_{\mathrm{NO}} - \mu_{\mathrm{O}}$. To avoid the formation of competing secondary phases, i.e. solids Zr and Ti, and compounds ZrO_2, ZrN, TiO_2 and TiN, we require $\mu_{\mathrm{M}} \leq E_{\mathrm{M}}(\mathrm{bulk})$, $\mu_{\mathrm{M}} + 2\mu_{\mathrm{O}} \leq \Delta H_f(\mathrm{MO}_2)$ and $\mu_{\mathrm{M}} + \mu_{\mathrm{N}} \leq \Delta H_f(\mathrm{MN})$, where M = (Zr, Ti). We find that, for both sources of nitrogen, μ_{M} obtained by its nitride has the lowest value, thus is used to present our results for the co-doped systems. For the single dopants, μ_{M} is obtained by its oxides. The experimental heat of formation[29] (-0.24 eV) for Zn_3N_2 indicates this phase is only weakly stable and moreover Zn_3N_2 is not observed experimentally, we, therefore, don't consider the possible formation of this phase.

To determine whether it is energetically preferred that two dopants bind, e.g. $\mathrm{Zr}_{\mathrm{Zn}}$ and N_{O}, in the neutral charge state, we calculate the binding energy which is defined as,

$$E_{\mathrm{b}} = E_{\mathrm{tot}}(\mathrm{Zr}_{\mathrm{Zn}} - \mathrm{N}_{\mathrm{O}}) + E_{\mathrm{tot}}(\mathrm{ZnO}) - E_{\mathrm{tot}}(\mathrm{Zr}_{\mathrm{Zn}}) - E_{\mathrm{tot}}(\mathrm{N}_{\mathrm{O}}), \tag{2}$$

where $E_{\text{tot}}(\text{Zr}_{\text{Zn}} + \text{N}_{\text{O}})$, $E_{\text{tot}}(\text{Zr}_{\text{Zn}})$ and $E_{\text{tot}}(\text{N}_{\text{O}})$ are the total energy for supercells containing defects $\text{Zr}_{\text{Zn}} - \text{N}_{\text{O}}$, Zr_{Zn}, and N_{O}, respectively. Negative E_{b} indicates the defect pair tends to bind to each other when both are present in the system. Extension of Eq. (2) to other complexes and charged states is straightforward.

Using the mixed scheme[30], the transition energy level of an acceptor with respect to the VBM is obtained by,

$$\epsilon(0/q) = [\epsilon_D^\Gamma(0) - \epsilon_{VBM}^\Gamma(\text{host})] + [\text{E}(\alpha, q) - (\text{E}(\alpha, 0) - q\epsilon_D^k(0))]/(-q), \qquad (3)$$

where $\epsilon_D^k(0)$ and $\epsilon_D^\Gamma(0)$ are the defect level at the special $\mathbf{k}$-points (averaged) and at the Γ-point, respectively; and $\epsilon_{VBM}^\Gamma(\text{host})$ is the VBM energy of the supercell at the Γ-point. $E(\alpha, q)$ and $E(\alpha, 0)$ are the total energies for supercells containing defect α in the charge state q and in the neutral charge state, respectively.

III. RESULTS

A. Fundamental properties of bulk structures

In our previous study[31], we reported the physical properties of bulk ZnO, bulk Zn, the O_2 and N_2 molecules. All the calculated values are in good agreement with those obtained from other GGA calculations and experiments. We use an $8 \times 8 \times 8$ $\mathbf{k}$-point mesh for calculating bulk Zr, Ti, Y and Sc, where the physical properties are listed in Table I. It can be seen that our results compare very well with the experimental values. The physical properties of ZrO_2, ZrN, TiO_2, and TiN are also listed in Table I, along with the available experimental and/or other DFT-GGA values. The calculated lattice constants for ZrO_2 and TiO_2 are generally slightly larger than experimental (1 % on average), and the heats of formation are smaller ($\sim$ 6 % on average) than experiment. For the compounds ZrN and TiN, the lattice constants compare very well with the experimental values, and the heats of formation are in good agreement with a previous DFT-GGA investigation[38].

B. Single dopants/impurities

We consider substitutional Zr on the Zn site, Zr_{Zn}, since this is indicated experimentally in Zr-doped ZnO films[39,40], and the ionic radius of Zr^{4+} (0.745 Å) is very close to that of Zn^{2+} (0.74 Å). We find that Zr_{Zn} induces a fully occupied singlet defect state in the conduction band, and thus acts as a double donor in ZnO. For $\text{Zr}_{\text{Zn}}^{2+}$, the apical and planar distances between the Zr and the O atoms are 0.45 % and 1.04 % shorter than the values in bulk ZnO, respectively.

For Ti-doped ZnO, recent experimental reports show evidence that Ti atoms are more likely to substitute the Zn sites than to occupy interstitial sites[41], and it has been found by Hall-effect measurements[42] that Ti-doped ZnO films prepared by RF magnetron sputtering are n-type semiconductors. We find that a substitutional Ti on the Zn site also acts as a double donor with a doubly occupied singlet defect state in the conduction band, and thus contributes to the n-type conductivity. The Ti–O bonds along the c-axis and in the (0001) plane are shortened by 7.7 % and by 7.9 %, respectively, compared to the values in bulk ZnO. In a previous DFT-GGA calculation[43] where the experimental lattice constants were used with a smaller 32-atom supercell, the Ti–O bonds were found to be 4.5 % and 3.4 % shorter compared to the value of bulk ZnO.

The ionic radii of Sc and Y are close to that of Zn, suggesting that they may readily incorporate on Zn sites. Minami et $al.$[44] have shown evidence that a Sc or Y atom in Sc or Y doped ZnO films, prepared by d.c. magnetron sputtering, effectively acts as a donor when it occupies the Zn site. Based on our calculations, both the Y_{Zn} and the Sc_{Zn} defects induce a singly occupied level in the conduction band, and thus act as single donors, consistent with experiments. The Y_{Zn} dopant induces an increase in the distance of the single apical neighboring O atom of 7.8 % and of the nearest three planar O atoms by 6.4 % compared to the bulk ZnO values. The corresponding distances for Sc_{Zn} are only 0.3 % and 0.4 %, respectively, longer than the values in ZnO bulk. We perform spin-polarized calculations for the above four dopants in the neutral charge states, and find that all the systems are non-magnetic.

C. Co-doping with (Zr,N)

To obtain p-type ZnO using Zr and N co-doping, we follow the approach used in our previous work of co-doping (Al,N) and (Ga,N) in ZnO[31], where we have reported[31] for N occupying on the O site, N_{O}, an acceptor ionization energy of 0.33 eV. Since Zr is a double donor, and N is a single acceptor, in order to form a passivated stoichiometric complex, and create fully occupied impurity bands above the VBM of ZnO, two N acceptors would be required to bind to Zr_{Zn} to passivate one Zr donor. We consider a number of configurations (A, B, and C) of the neutral (Zr,N)

complex, including the Zr and N atoms located along the c-axis on the nearest neighbor sites [(Zr-N)-A], in the same (0001) plane on the nearest neighbor sites [(Zr-N)-B], and "far apart" ($\sim$9 Å) [(Zr-N)-C]. We find the most stable structure, as shown in Fig. 1(a), is the configuration A, where Zr and N bind together strongly with a binding energy of -2.07 eV, referenced to the neutral isolated Zr and N defects (as listed in Table II). Configurations B and C are about 0.03 eV and 0.67 eV higher in energy, respectively. The complex (Zr-N)-A induces a singly state in the conduction band which is occupied with on electron, and thus acts as a single donor. The binding energy of this structure in the 1+ charge state is -0.32 eV referenced to Zr_{Zn}^{2+} and N_O^-. In the 1+ charge state of this complex, the bond length of Zr–N is 1.99 Å, and the average distance between Zr and O is 2.03 Å, which is close to the average Zn–O bond length of 2.01 Å in bulk ZnO.

With further doping of N atoms, we consider the configuration [(Zr-2N)-A] where the second N is located on a nearest neighbor O site of the Zr atom, and the configuration [(Zr-2N)-B] where the second N atom is far apart from the complex (Zr-N)-A. We find the energy of configuration B is about 0.4 eV higher than the configuration A. Thus the additional N atom prefers to bind to the complex (Zr-N)-A. The Atomic structure of the [(Zr-2N)-A] complex in the neutral charge state is shown in Fig. 1(b). The binding energy of this complex is -1.48 eV with respect to the neutral [(Zr-N)-A] complex and an isolated N_O, and is -0.14 eV referenced to [(Zr-N)-A]$^+$ and N_O^-. The passivated complex (Zr-2N)-A induces a fully occupied impurity state above the VBM (we denote this fully occupied defect state as the "new VBM"). For the (Zr-2N)-A complex, the distance between Zr and N atoms are 2.02 Å along the c-axis and 2.01 Å in the (0001) plane. The bond length of Zr–O is 2.06 Å on average, and the average distance between N and Zn atoms is 1.98 Å.

If we consider that a further excess of nitrogen is present in the system, we find that additional N atoms slightly prefer to bind to the (Zr-2N) complexes rather than being isolated, forming a (Zr-3N) complex with three N atoms occupying the nearest-neighbor O sites of the Zr atom. The binding energy of this complex is -0.03 eV with respect to the neutral (Zr-2N)-A complex and an isolated N dopant. Thus the (Zr-2N) complex likes to bind with N atoms on nearest-neighboring O sites, but only through a very weak interaction. The relaxed structure for this configuration is shown in Fig. 1(c). The (Zr-2N):N system induces a singlet defect state with a hole above the new VBM, and acts as a single acceptor with an ionization energy of 0.08 eV (reference to the new VBM), which is lower than that (0.33 eV) of the isolated N acceptor. The average bond length of Zr–N is 2.04 Å, the distance between Zr and O is 2.07 Å. The average distance between N and its nearest neighbor Zn atoms is 1.98 Å.

We further consider the interaction between the (Zr-2N):N complex and another N dopant occupying the fourth nearest-neighbor O site of the Zr atom. The binding energy calculated with respect to the neutral (Zr-2N):N complex and a nitrogen dopant is 0.22 eV, indicating a repulsive interaction. Although unstable in the neutral charge state, the (Zr-4N) complex induces a defect state with two holes above the new VBM and acts as a double acceptor. The binding energies are about 0.10 eV in the 1− and 2− charge states, referenced to N_O^- and the (Zr-2N):N complex in the neutral and 1− charge states, respectively. With unstable binding energies in neutral and charged states, the (Zr-4N) complex is unlikely to form.

D. Co-doping with (Ti,N)

Similarly to the (Zr,N) donor-acceptor co-doping system, we also consider (Ti,N) co-doping of ZnO and compare the behavior of this system to that of (Zr,N). So far there has been no successful experimental studies involving Ti and N co-doping in ZnO, nor any theoretical investigations. We find that Ti_{Zn} and N_O dopants prefer to be located along the c-axis on nearest neighbor sites, where the binding energy is -2.22 eV, relative to the single (neutral) Ti and N dopants. The configuration with Ti and N dopants occupying the nearest neighbor sites in the same (0001) plane is only marginally less (0.001 eV) stable. For comparison, the total energy of the configurations with Ti and N dopants far apart ($\sim$9 Å) is 0.82 eV higher. We therefore only further study the configuration with dopants positioned along the c-axis. The (Ti-N) complex acts as a single donor and induces a singly occupied defect state in the conduction band. The binding energy of this complex in the 1+ charge state is -0.58 eV referenced to Ti_{Zn}^{2+} and N_O^-. The Ti-N bond length is 1.84 Å, which is 8.5 % shorter than the average Zn–O bond length in bulk ZnO, and the average distance between Ti and its nearest neighbor O atoms is 1.90 Å, 5.5 % shorter than the corresponding values in bulk ZnO.

We also consider the complexes consisting of one Ti and two N atoms occupying nearest neighbor sites of the Ti dopant. We find the binding energy of the (Ti-2N) complex is -1.61 eV, with respect to the neutral (Ti-N) complex and N_O. The binding energy is -0.38 eV, relative to (Ti-N)$^+$ and N_O^-. As expected, the passivated complex (Ti-2N)-A induces a fully occupied impurity state above the VBM (which we call the "new VBM"). For this (Ti-2N) complex, the apical and planar Ti–N bond lengths are 1.87 Å and 1.88 Å, respectively. The bond length of Ti–O is 1.93 Å on average, and the average distance between N and Zn atoms is 1.99 Å.

With additional nitrogen, we find that the N atom prefers to be at the nearest neighbor site of the (Ti-2N)-A

complex. The resulting binding energy is -0.12 eV. This indicates that the complex (Ti-3N) is favorable with respect to the neutral (Ti-2N) complex and an isolated N dopant. This (Ti-2N):N configuration induces a singlet defect state with a hole above the new VBM, and thus acts as a single acceptor. The transition energy level from the neutral to $1-$ charge state is 0.09 eV above the new VBM. The binding energy of the (Ti-2N):N complex in the $1-$ charge state is -0.22 eV relative to the neutral (Ti-2N) complex and an isolated N dopant in the $1-$ charge state. The average Ti–N bond length is 1.91 Å (1.91 Å), the average distance between Ti and O atoms is 1.95 Å (1.96 Å), and the average bond length of Zn–N is 1.99 Å (1.98 Å).

We further consider the interaction between the (Ti-3N) configuration and a N atom located on the fourth nearest neighbor O site of the Ti atom, and find that the binding energy of the cluster (Ti-4N) is 0.18 eV (unbound), relative to neutral (Ti-3N) and N_O. The (Ti-4N) configuration acts as a double acceptor with two holes in a singlet defect state above the new VBM. This cluster is unstable in the neutral charge state and has a $(2-/-)$ transition at 0.07 eV with respect to the new VBM. The binding energy of this complex changes to -0.06 eV (stable) in the $-$ charge state, with respect to the neutral (Ti-3N) complex and N_O^-. In the $2-$ charge state, the binding energy is -0.09 eV (stable) referenced to (Ti-2N):N and N_O in their $-$ charge states. This indicates that the activated (Ti-3N) complex likes to bind with the activated N acceptor in ZnO. In the $-$ and $2-$ charge states, the average Ti–N bond lengths are 1.93 Å, and the average distance between N and Zn atoms is 1.98 Å and 1.97 Å, respectively.

E.   Co-doping of Y or Sc and N

Yttrium and Sc have a similar electronic structure to Ti and Zr except that they have one electron less. It is possible therefore that one Y (Sc) atom and one N atom may form a passivated complex, which may create fully occupied impurity bands above the VBM of ZnO and hence offer improved incorporation and activation of nitrogen.

We now consider the configuration (A) with Y (Sc) and N atoms located along the c-axis, the configuration (B) with Y (Sc) and N atoms located in the same (0001) plane, and the configuration (C) with Y (Sc) and N atoms located as far as possible in the supercell. We find that configuration A is the most stable configuration, the total energy difference between the configuration A and B is 0.07 eV and 0.03 eV for the complexes (Y-N) and (Sc-N), respectively. The configuration C has the highest total energy for both co-doped systems. For further study, we therefore only consider the configurations (Y-N)-A and (Sc-N)-A. The binding energies of the complex (Y-N)-A is -1.06 eV, referenced to the neutral Y_{Zn} and N_O, The results indicate that there is an attractive interaction between the neutral Y_{Zn} and N_O defects. The complex (Sc-N)-A exhibits a similar behavior. In particular, the binding energies of this complex is -1.19 eV, relative to the neutral Sc_{Zn} and N_O.

Based on the (Y-N)-A and (Sc-N)-A complexes, we add a second N at a nearest neighbor O site of the Y [(Y-N):N-A] and Sc atoms [(Sc-N):N-A], and at a "far apart" position from (Y-N)-A and (Sc-N)-A complexes, to check if these configurations may be stable. We find that the calculated binding energies for neutral "far apart" configurations are -0.08 eV and -0.06 eV, respectively, and the values for neutral (Y-N):N-A and (Sc-N):N-A complexes are positive at 0.25 eV and 0.19 eV, respectively. This can be understood in that the N–Zn bond is stronger than the N–Y or N–Sc bond, which is consistent with our calculations which show that N–Zn bonds are shorter than the Zn–O bond, but that the N–Y or N–Sc is longer than the Zn–O bond length. Our calculations suggest that clusters with high number of N is unlikely in Y and Sc doped systems.

IV.   FORMATION ENERGIES AND TRANSITION ENERGY LEVELS

Figure 2 shows the calculated total DOS for the bulk ZnO host (red curve) and a supercell containing a complex (black curve) of (a) (Zr-2N), (b) (Ti-2N), (c) (Y-N) and (d) (Sc-N) (d). It can be seen that the formation of passivated complexes does not change the basic electronic structure, but only generates an additional fully occupied defect band above the VBM. When excess N atoms are available, they will dope the passivated system. The transition will occur between the N defect levels and the fully occupied impurity bands, rather than the valence bands of bulk ZnO. In the (Zr-2N):N and (Ti-2N):N systems, the calculated ionization energies are 0.08 eV and 0.09 eV, respectively. In the (Y-N):N and (Sc-N):N systems, the calculated ionization energies are 0.14 eV and 0.18 eV, respectively.

In Fig. 3 the formation energies of the isolated dopants and complexes are shown as a function of the Fermi level, E_F, under Zn-rich conditions and with different nitrogen gas sources, the N_2O source (a) and the NO source (b). We include the formation energies for the (Ga,N) co-doping system from our previous study[31] for comparison, since co-doping ZnO with (Ga,N) has so far produced experimentally the best p-type co-doped ZnO[10,31,45,46]. It can be seen that in the neutral charge state the N dopant has a formation energy of 0.02 eV (-2.24 eV) with the N_2O (NO) source. This is consistent with a previous DFT investigation[47] which showed that the formation energy of the N acceptor is much lower when using a NO source than with a N_2O source. The very low value of the formation

energy of N_O when using a NO source suggests a good incorporation of nitrogen. However, recent experiments have shown that the fabricated p-type film is only metastable, and it converts to n-type with time[48]. 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 an oxygen vacancy which is also a donor.

Under oxygen-rich conditions, Zr and Ti donors have low formation energies, and thus contribute to the n-type conductivity. Experimentally, high quality n-type ZnO has been achieved by doping with these two elements[42,49].

For the co-doped systems, the (Zr-2N) or (Ti-2N) complex has a tendency to attract N in the (Zr-2N):N or (Ti-2N):N system with N atoms on the nearest-neighbor O sites, forming (Zr-3N) and (Ti-3N) clusters. The formation of the (Ti-4N) cluster can also be stable[50] The transition levels $(-/0)$ of (Zr-2N):N and (Ti-2N):N complexes, and the transition level $(2-/-)$ of (Ti-4N), are significantly lower than the value of the isolated nitrogen acceptor. For both N_2O and NO gas sources of nitrogen, (Ti-2N):N and (Zr-2N):N complexes have lower formation and ionization energies than the corresponding values of the (Ga-N):N system, thus may improve the prospect of p-type doping. We therefore predict that (Ti,N) co-doping, with similar formation and ionization energies to (Zr,N) co-doping, but with greater binding energies of the acceptor complexes, is more suitable for achieving p-type ZnO. And both the lower formation energies and lower ionization levels indicate that (Ti,N) co-doping is likely to yield better p-type conductivity than (Ga,N) co-doping[52].

V. CONCLUSION

We have studied the electronic and structural properties of Zr, Ti, Y and Sc co-doped with N in wurtzite ZnO via first-principles density-functional theory calculations. The substitutional Ti and Zr on Zn sites act as double donors, while substitutional Y and Sc act as single donors. Both of Zr and Ti donors exhibit a strong attractive interaction with a nitrogen atom located on the nearest-neighbor oxygen site, forming single donor complexes (Zr-N) and (Ti-N). Introducing a higher concentration of N results in the formation of passivated (Zr-2N) and (Ti-2N) complexes which induce fully occupied impurity bands above the VBM of bulk ZnO. Further doping of N in the (Zr-2N) and (Ti-2N) systems result in (Zr-2N):N and (Ti-2N):N systems which have ionization energies of 0.08 eV and 0.09 eV, respectively, notably lower than the isolated N acceptor (0.33 eV). Under different experimental conditions (i.e using an N_2O or NO source for the nitrogen atoms), the formation energies and transition levels of the (Ti-2N):N and (Zr-2N):N systems are lower than the (Ga-N):N systems. We, therefore, predict that (Ti,N) co-doping, as well as (Zr,N) co-doping, with both the lower formation energies and lower ionization levels, is likely to yield better p-type conductivity than (Ga,N) co-doping. Experiments are called for to investigate this prediction.

ACKNOWLEDGMENTS

[1] S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, J. Vac. Sci. Technol. B **22**, 932 (2004).

[2] A. Janotti and C. G. de Walle, Phys. Rev. B **76**, 165202 (2007).

[3] S. Choopun, R.D. Vispute, W. Noch, A. Balsamo, R.P. Sharma, T. Venkatesan, A. Iliadis, and D.C. Look, Appl. Phys. Lett. **75** 3947 (1999).

[4] T. Aoki, Y. Hatanaka, and D.C. Look, Appl. Phys. Lett. **76**,3257 (2000).

[5] J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu, and L. D. Chen, Appl. Phys. Lett. **84**, 541 (2004).

[6] M. Sanmyo, Y. Tomita, and K. Kobayashi, Chem. Mater. **15**, 819 (2003).

[7] C. J. Park, S. B. Zhang, and S.-H. Wei, Phys. Rev. B **66**, 073202 (2002).

[8] Using the Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional, the calculated N_O $(-/0)$ acceptor level is much deep, about 1.3 eV above the VBM [see, e.g., J. L. Lyons, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. 95, 252105 (2009)] This is because the HSE calculated N_O wavefunction is much more localized and it causes a large splitting between the occupied and unoccupied neutral N_O defect levels. Further quantitative experimental investigations of the N_O acceptor level would be most valuable.

[9] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **36**, L180 (1997).

[10] M. Joseph, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys. **38**, L1205 (1999).

[11] H. P. He, F. Zhuge, Z. Z. Ye, L. P. Zhu, F. Z. Wang, B. H. Zhao, and J. Y. Huang, J. Appl. Phys. **99**, 023503 (2006).

[12] A. Tsukazaki, H. Saito, K. Tamura, M. Ohtani, H. Koinuma, M. Sumiya, S. Fuke, T. Fukumura, and M. Kawasaki, Appl. Phys. Lett. **81**, 235 (2002).

[13] G. W. Cong, W. Q. Peng, H. Y. Wei, X. X. Han, J. J. Wu, X. L. Liu, Q. S. Zhu, Z. G. Wang, J. G. Lu, Z. Z. Ye, L. P. Zhu, H. J. Qian, R. Su, C. H. Hong, J. Zhong, K. Ibrahim, and T. D. Hu, Appl. Phys. Lett. **88**, 062110 (2006).

[14] L. L. Chen, J. G. Lu, Z. Z. Ye, Y. M. Lin, B. H. Zhao, Y. M. Ye, J. S. Li, and L. P. Zhu, Appl. Phys. Lett. **87**, 252106 (2005).

[15] G. D. Yuan, Z. Z. Ye, L. P. Zhu, Q. Qian, B. H. Zhao, R. X. Fan, C. L. Perkins, and S. B. Zhang, Appl. Phys. Lett. **86**, 202106 (2005).

[16] M. Kumar, T.-H. Kim, S.-S. Kim, and B.-T. Lee, Appl. Phys. Lett. **89**, 112103 (2006).

[17] K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger, and S. Niki, Appl. Phys. Lett. **79**, 4139 (2001); J. Cryst. Growth **237-239**, 503 (2002).

[18] Y. I. Alivov, D. C. Look, B. M. Ataev, M. V. Chukichev, V. V. Mamedov, V. I. Zinenko, Yu. A. Agafonov, and A. N. Pustovit, Solid-State Electron. **48**, 2343 (2004).

[19] T. Ohshima, T. Ikegami, K. Ebihara, J. Asmussen, and R. Thareja, Thin Solid Films **435**, 49 (2003).

[20] It is well known that all the oxides have a low VBM on an absolute scale because the VBM is derived from the oxygen p orbital which has very low energy. In our approach, the purpose is not make it less low (which could be done by adding Cu), the purpose is to use N+TM to form a defect band and using extra N to dope the N derived defect bands, so to make the ionization level shallower.

[21] Y. Yan, J. Li, S. Wei, and M. Al-Jassim, Phys. Rev. Lett. **98**, 135506 (2007).

[22] J. B. Li, S. H. Wei, S. S. Li, and J. B. Xia, Phys. Rev. B **74**, 081201 (2006).

[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[24] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org.

[25] C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).

[26] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).

[27] S.-H. Wei, Comp. Mater. Sci. **30**, 337 (2004).

[28] H. Kim, A. Cepler, M. S. Osofsky, R. C. Y. Auyeung, and A. Piqué, Appl. Phys. Lett. **90**, 203508 (2007).

[29] J. A. Dean, *Lange's Handbook of Chemistry*, 12th ed. (McGraw Hill, New York, 1979).

[30] Y. Yan and S. H. Wei, Phys. Stat. Sol. b **245**, 641 (2008).

[31] X. M. Duan, C. Stampfl, M. M. M. Bilek, and D. R. McKenzie, Phys. Rev. B **79**, 235208 (2009).

[32] *CRC Handbook of Chemistry and Physics*, 88th ed., edited by D.R. Lide (CRC Press, Boca Raton, FL, 2007-2008).

[33] C. Kittel, *Introduction of Solid State Physics* (Wiley, New York, 1986).

[34] A **k**-point mesh of $6 \times 6 \times 6$ is used for the calculations of monoclinic ZrO_2 and rutile TiO_2; and a **k**-point sampling of $8 \times 8 \times 8$ is used for the calculations of rocksalt ZrN and TiN. All the lattice constants are fully optimized.

[35] C. T. Lynch, *Handbook of Materials Science* (CRC Press, Cleveland, 1974).

[36] D. R. Lide, *CRC Handbook of Chemistry and Physics*, 83rd ed. (Boca Raton, FL 2002).

[37] W. B. Pearson, *Structure Reports*, (International Union of Crystallography, Oosthoek, Scheltema, and Holkema, Utrecht, 19131993).

[38] C. Stampfl, W. Mannstadt, R. Asahi, and A. J. Freeman, Phys. Rev. B **63**, 115106 (2001).

[39] M. Lv, X. Xiu, Z. Pang, Y. Dai, L. Ye, C. Cheng, and S. Han, Thin Solid Films **516**, 2017 (2008).

[40] G. K. Paul, S. Bandyopadhyay, S. K. Sen, ans S. Sen, Mater. Chem. Phys. **79**, 71 (2003).

[41] J. J. Lu, Y. M. Lu, S. I. Tasi, T. L. Hsiung, H. P. Wang, and L. Y. Wang, Optical Mater. **29**, 1548 (2007).

[42] Y. R. Park and K. J. Kim, Solid State Commun. **123**, 147 (2002).

[43] K. Osuch, E. B. Lombardi, and W. Gebicki, Phys. Rev. B **73**, 075202 (2006).

[44] T. Minami, T. Yamamoto, and T. Miyata, Thin Solid Films **366**, 63 (2000).

[45] D. C. Look and B. Claflin, Phys. Status Solidi B **241**, 624 (2004).

[46] J. Wang, E. Elamurugu, N. Barradas, E. Alves, A. Rego, G. Gonalves, R. Martins, and E. Fortunato, J. Phys. Condens. Matter **20**, 075220 (2008).

[47] Y. Yan and S. B. Zhang, Phys. Rev. Lett. **86**, 5723 (2001).

[48] X. Li, Y. Yan, T. A. Gessert, C. DeHart, C. L. Perkins, D. Young, and T. J. Coutts, Electrochem. Solid State **6**, c56 (2003).

[49] H. Kim, S. J. Horwitz, W. H. Kim, S. B. Qadri, and Z. H. Kafafi, Appl. Phys. Lett. **83**, 3809 (2003).

[50] We note that formation of the TM-N complexes is expected to readily occur given the large binding energy (between 1 and 2 eV), which is sufficient to overcome entropy effects, and that recent experiments indicate that N atoms diffuse readily in undoped ZnO, partially substituting for oxygen sites of ZnO[51]. For the complexes involving TM bound to three and four N atoms, where the binding energies are smaller, it is possible that entropy effects may prevent their formation, depending on the temperature and concentration.

[51] J. Lee, J. Ha, J. Hong, S. Cha, and U. Paik, .J. Vac. Sci. Tech. B 26, 1696 (2008).

[52] We note that it is expected that the transport in the defect bands is not optimal, which is also true in most pure oxides which have large hole effective masses due to the localized oxygen p-orbital. However, the focus of this paper is to using a novel approach to generate charge carriers by reducing the defect ionization energy for a system that has almost no carrier ionization. In this case, the problem of a large effective mass will be secondary and can be partially overcome by increasing the dopant concentration.

TABLE I: Calculated lattice constants, a, b, c, (in Å) and the cohesive energy, E_c, and the heat of formation, ΔH, (in eV) for bulk systems. The experimental and/or other DFT-GGA values are included for comparison.

Crystal		a	b	c	β	E_c	ΔH
Zr	present	3.228		5.132		−6.43	
	experiment[a]	3.232		5.149		−6.25[b]	
Ti	present	2.913		4.713		−5.28	
	experiment[a]	2.951		4.719		−4.85[b]	
Y	present	3.620		5.781		−4.27	
	experiment[a]	3.648		5.731		−4.37[b]	
Sc	present	3.286		5.297		−4.18	
	experiment[a]	3.309		5.268		−3.90[b]	
ZrO_2	present[c]	5.200	5.262	5.331	99.46	−21.61	−10.28
	experiment[a]	5.145	5.205	5.311	99.23	−22.85[d]	−11.18[a]
TiO_2	present[c]	4.632		2.969		−21.03	−9.10
	experiment[a]	4.594		2.962		−19.90[e]	−9.59[a]
ZrN	present[c]	4.599					−3.56
	experiment[f]	4.537					
	DFT-GGA[g]	4.57					−3.82
TiN	present[c]	4.244					−3.58
	experiment[f]	4.242					
	DFT-GGA[g]	4.26					−3.56

[a] Reference 32
[b] Reference 33
[c] Reference 34
[d] Reference 35
[e] Reference 36
[f] Reference 37
[g] Reference 38

TABLE II: The binding energies, E_b, in eV, for the defect complexes in ZnO. The binding energies of the defects are computed with respect to the defect combinations in the parentheses. Note, for simplicity, for complexes without using a subscript, N atoms always occupy O site, and transition metals occupy Zn sites.

Defect	E_b		Defect	E_b	
Zr-N	-2.07	$(Zr_{Zn} + N_O)$	Ti-N	-2.22	$(Ti_{Zn} + N_O)$
$(Zr\text{-}N)^+$	-0.32	$(Zr_{Zn}^{2+} + N_O^-)$	$(Ti\text{-}N)^+$	-0.58	$(Ti_{Zn}^{2+} + N_O^-)$
Zr-2N	-1.48	$[(Zr\text{-}N)+N_O)]$	Ti-2N	-1.61	$[(Ti\text{-}N)+N_O)]$
Zr-2N	-0.14	$[(Zr\text{-}N)^++N_O^-]$	Ti-2N	-0.38	$[(Ti\text{-}N)^++N_O^-]$
Zr-3N	-0.03	$[(Zr\text{-}2N)+N_O)]$	Ti-3N	-0.12	$[(Ti\text{-}2N)+N_O)]$
$(Zr\text{-}3N)^-$	-0.02	$[(Zr\text{-}2N)+N_O^-)]$	$(Ti\text{-}2N){:}N^-$	-0.22	$[(Ti\text{-}2N)+N_O^-)]$
Zr-4N	0.22	$[(Zr\text{-}3N)+N_O)]$	Ti-4N	0.18	$[(Ti\text{-}3N)+N_O)]$
$(Zr\text{-}4N)^-$	0.10	$[(Zr\text{-}3N)+N_O^-)]$	$(Ti\text{-}4N)^-$	-0.06	$[(Ti\text{-}3N)+N_O^-)]$
$(Zr\text{-}4N)^{2-}$	0.10	$[(Zr\text{-}3N)^-+N_O^-]$	$(Ti\text{-}4N)^{2-}$	-0.09	$[(Ti\text{-}3N)^-+N_O^-]$
Y-N	-1.06	$(Y_{Zn} + N_O)$	Sc-N	-1.19	$(Sc_{Zn} + N_O)$
Y-2N	0.25	$(YN+N_O)$	Sc-2N	0.19	$[(Sc\text{-}N)+N_O)]$
$(Y\text{-}2N)^-$	0.41	$(YN+N_O^-)$	$(Sc\text{-}N){:}N^-$	0.18	$[(Sc\text{-}N)+N_O^-)]$

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

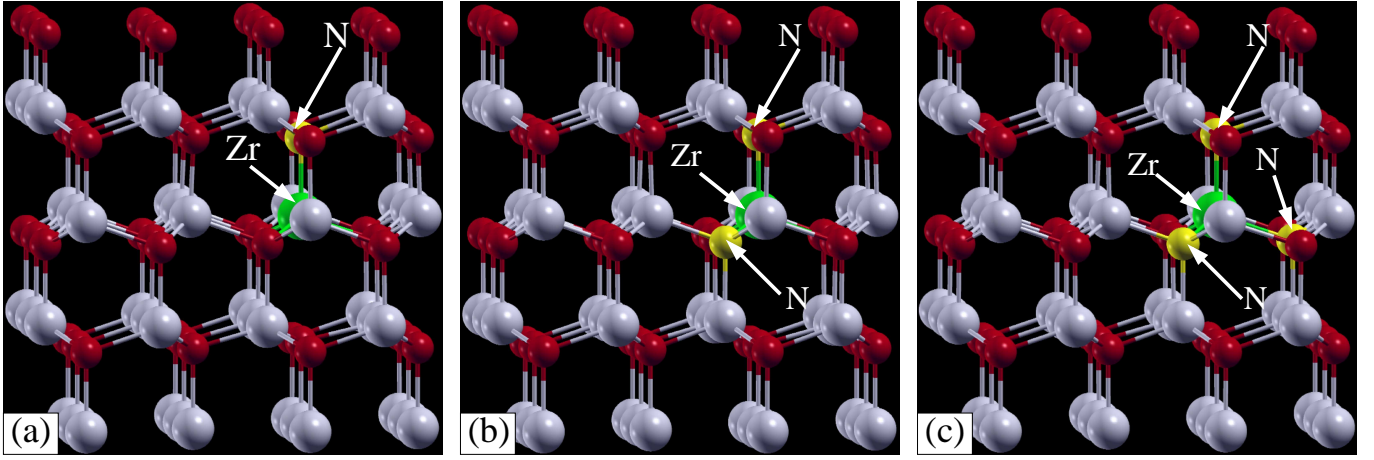| Defect	$\epsilon(-/0)$	$\epsilon(2-/-)$
N_O	0.33	
(Y-N):N	0.14	
(Sc-N):N	0.18	
(Zr-2N):N	0.08	
(Ti-2N):N	0.09	
(Ti-2N):2N	-	0.07

FIG. 1: (Color online) Atomic geometry of the relaxed structure in ZnO of (a) the (Zr-N), (b) the (Zr-2N), and (c) the (Zr-3N) configurations in the neutral charge state. The light grey and dark grey (red) spheres represent Zn and O atoms, respectively. The Zr (green) and N (yellow) atoms are indicated by the arrows.
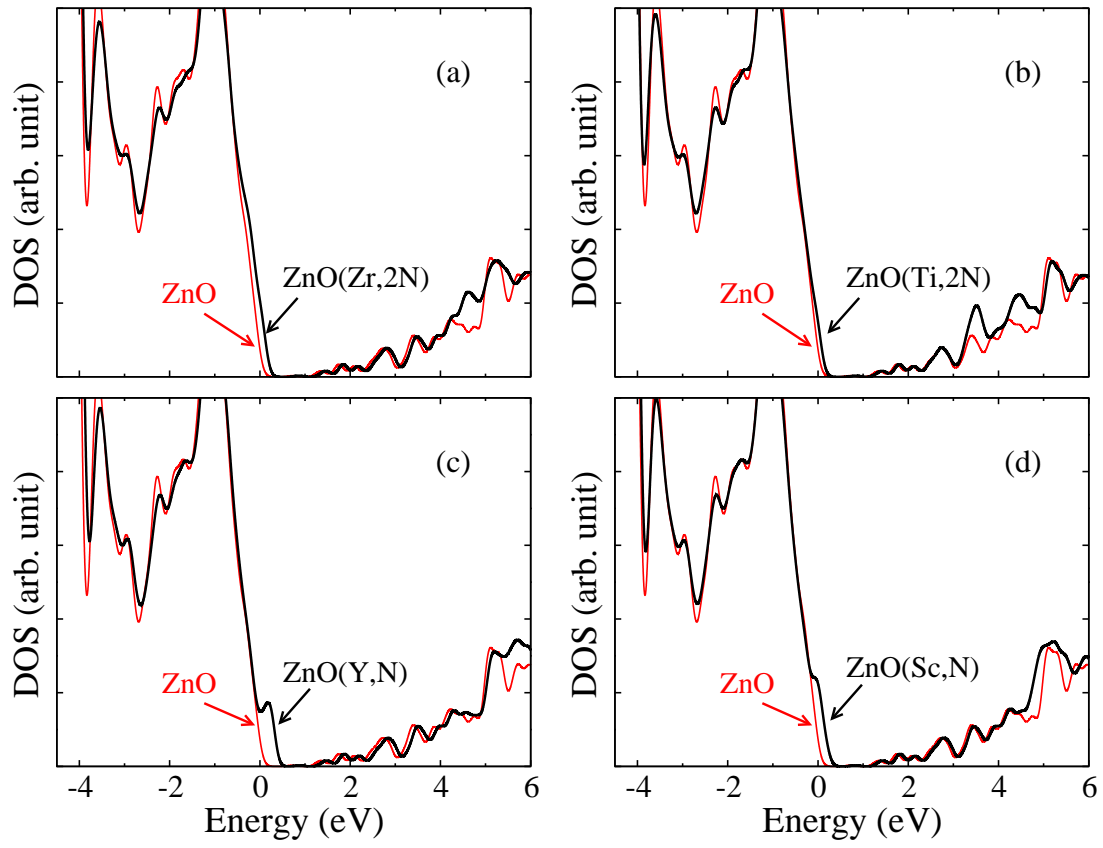
FIG. 2: (Color online) Calculated density-of-states for bulk ZnO shown in the thin (red) curves and for supercells containing (a) a (Zr-2N) complex, (b) a (Ti-2N) complex, (c) a (Y-N) complex, and (d) a (Sc-N) complex shown as the thick (black) curves.
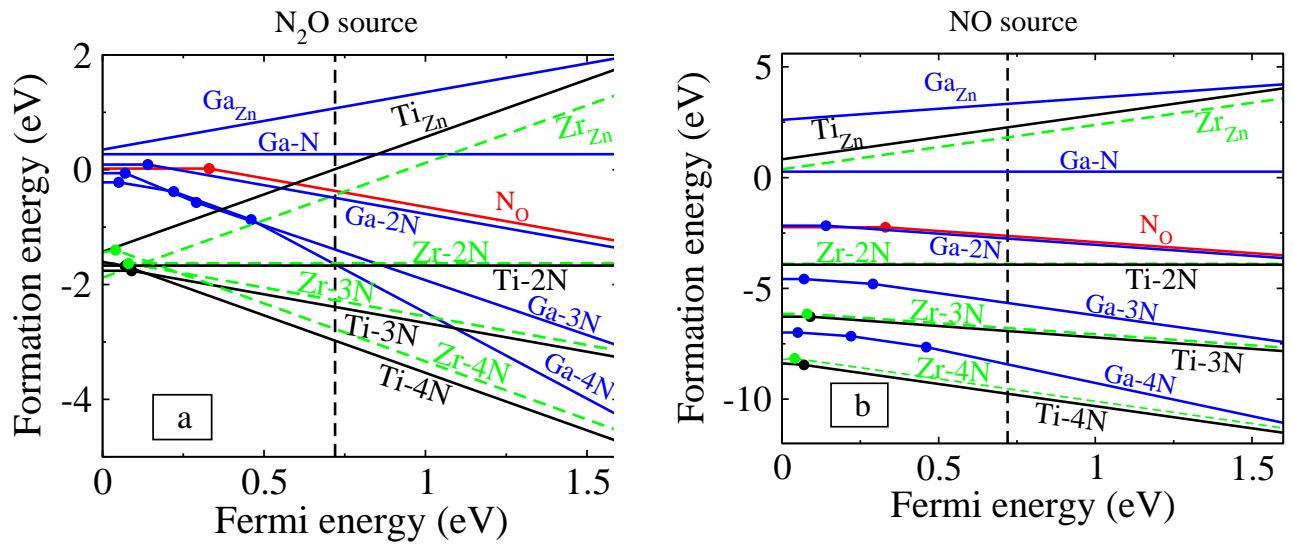
FIG. 3: (Color online) Formation energies as a function of the Fermi level for defects and complexes in wurtzite ZnO under Zn-rich conditions for (a) using N_2O as the source of nitrogen and (b) using NO as the source of nitrogen. The vertical dashed lines represent the calculated band gap of bulk ZnO. The kinks correspond to the transition levels (denoted by solid dots). Results for the Ga donor and complexes with (Ga,N) co-doping are from Ref. [31] and included for comparison.