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First-principles Study on Neutral Nitrogen Impurities in Zinc Oxide

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(Dated: Received on July 7, 2011; Accepted on August 19, 2011)

The atomic geometries, electronic structures, and formation energies of neutral nitrogen impurities in ZnO have been investigated by first-principles calculations. The nitrogen impurities are always deep acceptors, thus having no contributions to p-type conductivity. Among all the neutral nitrogen impurities, nitrogen substituting on an oxygen site has the lowest formation energy and the shallowest acceptor level, while nitrogen substituting on a zinc site has the second-lowest formation energy in oxygen-rich conditions. Nitrogen interstitials are unstable at the tetrahedral site and spontaneously relax into a kick-out configuration. Though nitrogen may occupy the octahedral site, the concentrations will be low for the high formation energy. The charge density distributions in various doping cases are discussed, and self-consistent results are obtained.

Key words: First-principles, ZnO, Nitrogen, Doping

I. INTRODUCTION

ZnO is a promising semiconductor material for its direct and wide band gap. It has attracted much attention for its possible applications in optoelectronic devices such as lasers and light emitting diodes [1–3]. However, ZnO crystal is almost always n-type, and its applications are hindered by the difficulty of making reproducible low resistivity p-type ZnO. To obtain p-type ZnO, acceptor doping is necessary, among which nitrogen (N) is usually considered to be a kind of promising dopant. In recent years, the realization of p-type ZnO with hole concentrations of 10^{17} – 10^{19} cm⁻³ in experiment has been reported [4–6]. On the other hand, theoretical studies on nitrogen impurities in ZnO are also widely performed, especially by first-principles calculations. Lee *et al.* pointed out that nitrogen acceptors in ZnO would be compensated by various impurities or defects [7]. However, Fon *et al.* argued that nitrogen atoms would incorporate on oxygen sites, where they were expected to act as acceptors [8]. Besides the mono-doping, codoping studies such as B–N [9], Al–N [10–13], Ga–N [14], In–N [15, 16], and Zr–N [17] have also been performed by first-principles calculations. Especially, Limpijumnong *et al.* studied the behaviors of group-V elements such as As and Sb [18], and some substitutional diatomic molecules such as NO, N₂, and so on [19]. They found that nitrogen was more likely to form (N₂)²⁺ and (NO)²⁺, “thereby hindering the ef-

forts of doping ZnO p-type”. Though so much work has been done, we think that comprehensive investigations on nitrogen impurities in ZnO are still necessary.

In this work, we consider all the possible neutral nitrogen impurities in ZnO, including substitutional impurities, antisites, and interstitials. We discuss the atomic geometries, electronic structures, and formation energies in various doping cases.

II. MODEL AND METHOD

All calculations in this work are based on density functional theory (DFT). We use the generalized-gradient approximation (GGA) [20] and the projector-augmented wave (PAW) [21, 22] method as implemented in the VASP code [23–25].

Calculations for wurtzite ZnO primitive cell were carried out using a $9 \times 9 \times 6$ Monkhorst-Pack *k*-point mesh. The obtained lattice parameters ($a=b=319.9$ pm, $c=521.6$ pm) were in good agreement with the experimental values ($a=b=324.9$ pm, $c=520.6$ pm) [26], and we used them throughout our calculations. We find that a 32-atom supercell may introduce an energy error of about 0.5 eV. So in the present work, the results are obtained from a 72-atom supercell doping. A $2 \times 2 \times 2$ *k*-point mesh for the Brillouin zone integration. The energy cutoff was 520 eV, and the geometry relaxation tolerance was better than 0.05 eV/Å.

To calculate the nitrogen formation energy, an equation is defined as [27],

$$E^f(N, q) = E_t(N, q) + q\mu_e - n_{\text{Zn}}\mu_{\text{Zn}} - n_{\text{O}}\mu_{\text{O}} - n_{\text{N}}\mu_{\text{N}} \quad (1)$$

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TABLE I Impurity formation energies in units of eV.

Supercell		Impurity formation energies			
		N _O	N _{Zn}	N _{i^{oct}}	N _k
32 atoms	Zn-rich	0.68	6.80	6.39	4.25
	O-rich	4.12	3.28		
72 atoms	Zn-rich	1.10	7.08	6.83	4.44
	O-rich	4.62	3.56		
72 atoms (Spin polarized)	Zn-rich	0.63	6.17	5.53	3.63
	O-rich	4.15	2.65		

where $E_i(N, q)$ is the total energy of the supercell containing the nitrogen impurity in charge q . μ_e , μ_{Zn} , μ_O , and μ_N are the chemical potentials of electron, zinc, oxygen, and nitrogen, respectively. In this work, only the neutral charge state ($q=0$) is considered. The calculated formation enthalpy of ZnO is -3.52 eV, in good agreement with the experimental value of -3.6 eV [28]. N₂ is used as a dopant source, from which the chemical potential of nitrogen is determined.

III. RESULTS AND DISCUSSION

A. Atomic geometry and formation energy

In this work, we consider all the possible neutral nitrogen impurities in ZnO crystal: substitutional impurities, antisites, and interstitials. The calculated impurity formation energies are listed in Table I, in Zn-rich and O-rich conditions, respectively.

It can be seen from Table I that a 32-atom supercell can introduce an error of about 0.5 eV in energy, so the following results are based on the calculations of a 72-atom supercell, which can introduce an error only about 0.1 eV. Figure 1(a) shows the atomic geometry of perfect ZnO, while Fig.1 (b)–(e) show the local atomic geometries of various doping cases. Table II lists the relaxed geometric parameters, where O¹, O², Zn¹, Zn², stand for the atoms numbered from 1 to 4 in Fig.1.

When nitrogen substitutes on an oxygen site (N_O), the local geometry around the substitutional site has almost tetrahedral symmetry, as shown in Fig.1(b). This is because nitrogen atom is the closest in atomic size to oxygen, and therefore, the substitution results in a minimum strain in the crystal. Compared with pure ZnO, the four nearest-neighbor (NN) zinc atoms around N_O are displaced inward by 3.1% and 2.1% of the equilibrium O–Zn bond length along c and a axis, respectively. Compared with the O–Zn bond length, the changes of the N_O–Zn bond length can be explained by the differences of the electronic structures between nitrogen and oxygen atoms. Nitrogen has five valence electrons, while oxygen has six. Therefore, when nitrogen substitutes on an oxygen site, it can accept one more valence electron. This strengthens the interactions between ni-

TABLE II Geometric parameters of atomic distance and bond angle before and after nitrogen-doping.

Doping		Distance/Å		Angle/(°)
ZnO	O ⁴ –Zn ^{1,2,3}	1.94	O ² –Zn ⁴ –O ⁴	108.16
	O ⁴ –Zn ⁴	1.96		
N _O	N _O –Zn ^{1,2,3}	1.90	O ² –Zn ⁴ –N _O	110.85
	N _O –Zn ⁴	1.90		
N _{Zn}	N _{Zn} –O ¹	2.48	O ² –N _{Zn} –O ³	110.82
	N _{Zn} –O ^{2,3}	1.35		
	N _{Zn} –O ⁴	2.74		
N _{i^{oct}}	Zn ⁴ –O ^{2,3}	2.00	Zn ² –O ⁴ –Zn ³	102.77
	N _{i^{oct}} –Zn ⁴	2.03		
	N _{i^{oct}} –Zn ^{2,3}	2.35	O ² –Zn ⁴ –O ⁴	114.41
	Zn ⁴ –O ⁴	2.04		
N _k	N _k –Zn ^{1,3}	1.90	Zn ¹ –N _k –Zn ³	132.34
	N _k –O ⁴	1.32		
	O ⁴ –Zn ^{2,4}	1.95	N _k –O ⁴ –Zn ⁴	115.78

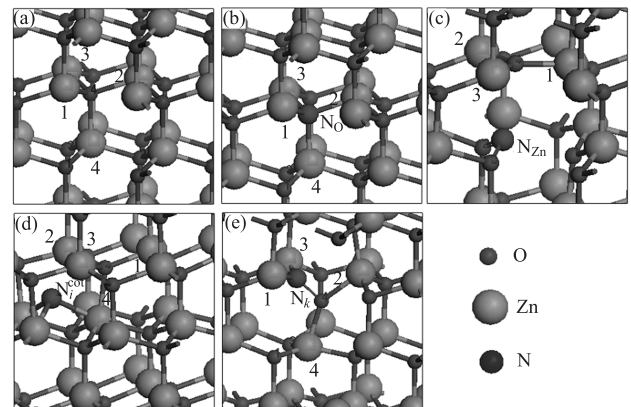


FIG. 1 Local atomic geometries in (a) perfect ZnO, (b) N_O, (c) N_{Zn}, (d) N_{i^{oct}} and (e) N_k cases. Atoms numbered from 1 to 4 are cited as Zn¹, Zn², Zn³, Zn⁴, or O¹, O², O³, and O⁴, respectively.

trogen and the NN zinc atoms. Thus, the N_O–Zn bond length is decreased, and the inward displacements of the NN zinc atoms around N_O take place. Besides, we note that among all the nitrogen impurities, N_O has the lowest formation energy, as shown in Table II. Therefore, it will occur in the highest concentrations, which is in agreement with the results of Fon *et al.* [8].

When nitrogen substitutes for a zinc atom (N_{Zn}), the local geometry around the substitutional site assumes a low symmetric configuration, as shown in Fig.1(c). From Table II, O² and O³ are equidistant from N_{Zn} by 1.35 Å. It is smaller than the sum of the covalent radii of nitrogen (0.75 Å) and oxygen (0.73 Å), indicating the formation of chemical bonds between O², O³, and N_{Zn}. According to our results, the bond angle O²–N_{Zn}–O³ is 110.82°. On the other hand, the distances of N_{Zn}–O¹ and N_{Zn}–O⁴ are large, 2.48 and 2.74 Å, respectively.

They are much larger than the sum of the covalent radii, so no chemical bonds are formed between O^1 , O^4 , and N_{Zn} . We note from Table I that the formation energy of N_{Zn} differs a lot from Zn-rich to O-rich conditions. In Zn-rich conditions, the formation energy of N_{Zn} is the highest, implying the lowest concentrations. However, in O-rich conditions, N_{Zn} has the second-lowest formation energy among all the doping cases. Thus, higher concentrations can also be expected for N_{Zn} in O-rich conditions. Despite of this, N_{Zn} impurities are usually neglected by previous studies.

Wurtzite ZnO has two distinct types of interstitial sites: the tetrahedral site and the octahedral site. According to our results, nitrogen atoms can be accommodated in the form of octahedral interstitials (N_i^{oct}). However, N_i^{oct} has high formation energy and introduces large relaxations to the NN atoms. It is displaced along the [0001] direction toward the basal plane formed by three oxygen neighbors, as shown in Fig.1(d). From Table II, the displacement increases the bond angle $O^2-Zn^4-O^4$ and decreases the bond angle $Zn^2-O^4-Zn^3$, compared with the case of perfect ZnO.

According to our results, nitrogen atom is unstable at the tetrahedral site, and it will spontaneously relax into a kick-out configuration (N_k), as shown in Fig.1(e). The nitrogen atom kicks O^4 out of its nominal lattice site and replaces it. Then O^4 shares the same lattice site with the nitrogen atom, assuming a split-like interstitial configuration. It should be noted that to be a native point defect, split-oxygen is also possible, as pointed out by Janotti and Walle [29, 30]. The calculated N_k-O^4 distance is 1.32 Å, smaller than the sum of the covalent radii, indicating the formation of the O- N_k chemical bond. However, because of the large size of the oxygen interstitial, Zn^4 , O^4 , and N_k are not in a line. According to our results, a bond angle of 115.78° can be expected. As discussed above, N_k can accept one more electron than oxygen. This increases the bonding interactions to the NN zinc atoms, thus decreasing the N-Zn bond length in the basal plane. From Table I, the formation energy of N_k is as high as 4.44 eV. This value is so high that the defects can not occur in high concentrations.

B. Electronic structures

We show the density of states (DOS) in Fig.2, and the charge density distributions in Fig.3 and Fig.4 for various doping cases. The DOS of perfect ZnO shown in Fig.2(a) is in good agreement with our previous studies [31]. From Fig.3(a), it is obvious that ionic bonds are formed between Zn and O atoms.

Compared with perfect ZnO crystal, different doping cases have different electronic structures. Nitrogen has five valence electrons, while oxygen has six. Therefore, N_O may accept one additional electron from the NN zinc atoms, thus acting as an acceptor. We can see from Fig.2(b) that a partially occupied impurity state ap-

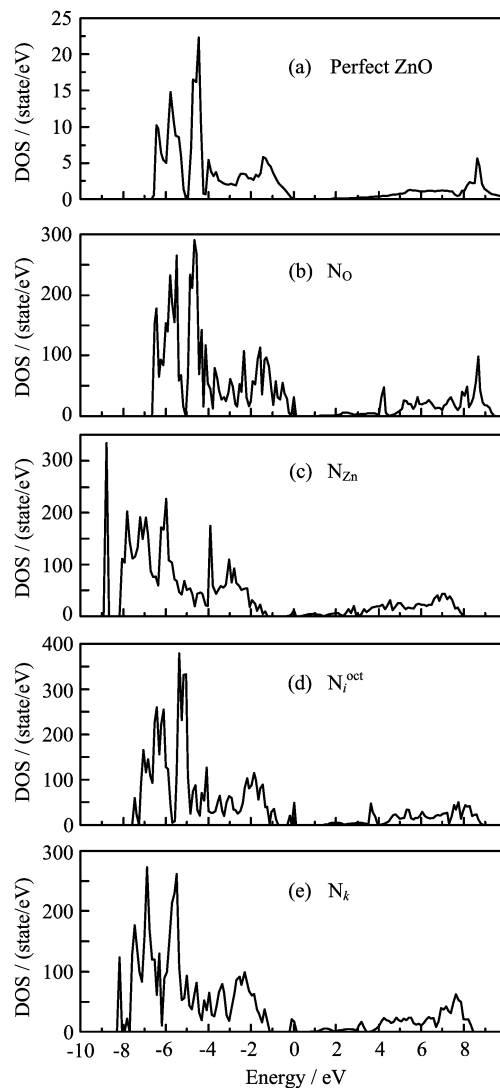


FIG. 2 Total density of states in (a) perfect ZnO, (b) N_O , (c) N_{Zn} , (d) N_i^{oct} , and (e) N_k cases. The zero energy is set at the Fermi-level.

pears near the valence band maximum (VBM). A comprehensive analysis of the electronic structures indicates that the state is mainly contributed by the nitrogen 2p state. Though N_O has the lowest formation energy (see Table I), it has a deep acceptor level. Therefore, N_O is unlikely to play any role in p-type conductivity, which is in agreement with the recent reports [32]. The chemical bonds between N_O and the NN neighbor zinc atoms are similar to the O-Zn bonds in perfect ZnO, as shown in Fig.3(b). This is because the electronic structures of nitrogen and oxygen are very close to each other, and so are their electro-negativities.

Figure 2(c) shows the DOS in N_{Zn} doping case. It can be seen from the figure that an impurity state appears near the VBM. A further analysis indicates that the state is mainly contributed by the nitrogen 2s state, and furthermore, it is already fully occupied. So this

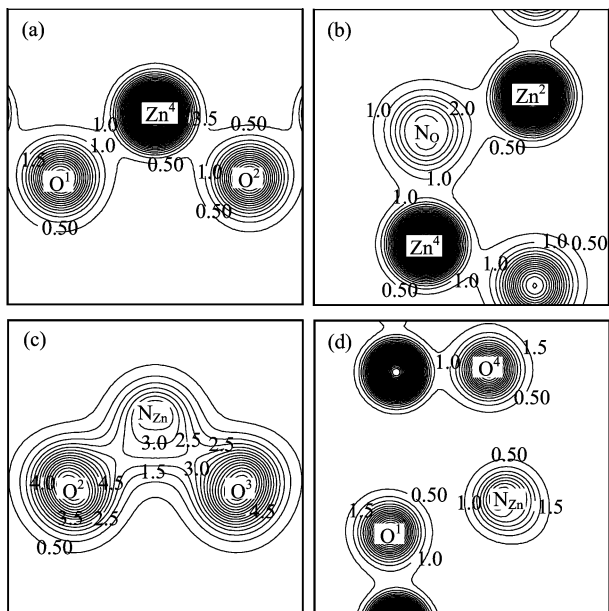


FIG. 3 Charge density distributions in (a) perfect ZnO, (b) NO , (c) N_{Zn} , and (d) N_{Zn} cases.

impurity state can not accept additional electrons, thus having no contributions to the p-type conductivity of ZnO. Besides, we can also see from the figure that a partially occupied impurity state occurs around the Fermi level. In fact, this state is mainly derived from the nitrogen 2p state. Obviously, it is so far from the VBM, making it unlikely to accept additional electrons from the valence band. Therefore, this state can not contribute to the p-type conductivity too. From Fig.3(c), strong chemical bonds with obvious covalent character are formed between O^2 , O^3 , and N_{Zn} . This is in agreement with the fact that the distances of $\text{N}_{\text{Zn}}-\text{O}^2$ and $\text{N}_{\text{Zn}}-\text{O}^3$ are smaller than sum of covalent radii. However, dangling bonds are formed on O^1 and O^4 atoms for the large $\text{N}_{\text{Zn}}-\text{O}^1$ and $\text{N}_{\text{Zn}}-\text{O}^4$ distances, as shown in Fig.3(d) and Table II.

We find that N_i^{oct} configuration has similar DOS to N_{Zn} configuration, as shown in Fig.2(d). First, an impurity state appears at the top of the VBM, which is mainly contributed by the nitrogen 2s state. Similarly, the state is fully occupied, thus having no contributions to the p-type conductivity. Secondly, two impurity peaks appear near the Fermi level. They are contributed by the nitrogen 2p state and partially occupied. However, it is obvious that these levels are too deep to contribute to the p-type conductivity. From Fig.4(a), one can judge that no chemical bonds are formed between N_i^{oct} and the zinc atoms in the basal plane containing Zn^2 and Zn^3 . On the contrary, chemical bonds are obviously formed between N_i^{oct} and the zinc atoms in the basal plane containing Zn^4 , as shown in Fig.4(b). These results are in agreement with the large $\text{N}_i^{\text{oct}}-\text{Zn}^{2,3}$ distance and the small $\text{N}_i^{\text{oct}}-\text{Zn}^4$ dis-

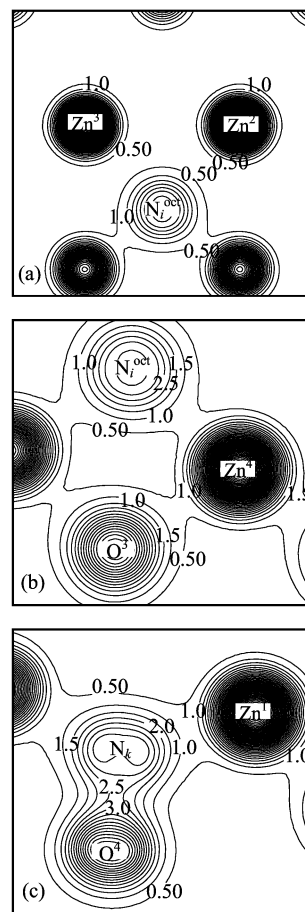


FIG. 4 Charge density distributions in (a) N_i^{oct} , (b) N_i^{oct} and (c) N_k cases.

tance listed in Table II.

As discussed, nitrogen is not stable at the tetrahedral site and it will spontaneously relax into a kick-out configuration. Figures 2(e) and 4(c) show the charge density and DOS of N_k configuration, respectively. In Fig.4, impurity states are located in the middle of the band gap. This state is derived from the nitrogen 2p state. However, it is a deep level, thus having no contributions to p-type conductivity. From the charge density map shown in Fig.4(c), it can be judged that the nitrogen atom forms strong covalent bonds with the neighbor oxygen atoms and strong ionic bonds with the neighbor zinc atoms.

C. Spin polarized calculations

Spin polarized calculations are also performed in the present work. We do not find any magnetic moments for the pure ZnO, and the atomic geometries are almost the same as those shown in Fig.1. However, when the dopants are introduced, the materials show ferromagnetic properties. The formation energy for spin polarized calculations is listed in Table I too, from which

we can judge that the ferromagnetic systems are energetically more stable. Because these energies are in qualitative agreement with the non-spin polarized ones, the discussions above will still apply here. We do not show the spin polarized DOS here for we are interested in the electric properties of doped ZnO.

IV. CONCLUSION

We have performed a first-principles study on the neutral nitrogen impurities in ZnO. According to our results, several conclusions can be drawn. (i) Nitrogen impurities always act as deep acceptors, so we do not think it is feasible to obtain p-type ZnO by nitrogen doping. (ii) Though N_O has the lowest formation energy, we should pay some attention to N_{Zn} in O-rich conditions. (iii) Nitrogen interstitials are unlikely to occur in high concentrations at the octahedral site for their high formation energy. (iv) Nitrogen interstitials at the tetrahedral site are unstable and spontaneously relax into a kick-out configuration.

V. ACKNOWLEDGMENTS

This work is supported by the Foundation for the Excellent Youth Scholars of Anhui Education Office (No.2012SQRL135), the National Natural Science Foundation of China (No.20903003), the Foundation for the Excellent Youth Scholars of Anhui Education Office (No.2009SQRZ097ZD), and the Foundation of Anhui Province Education Bureau (No.2006KJ270B).

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