Effects of Nitrogen Defect on Magnetism of Cu-doped InN: First-principles Calculations

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We investigate the electronic and magnetic properties in Cu-doped InN with the N vacancy (V_N) from first principles calculations. There is the long-range ferromagnetic order between two Cu atoms, attributed to the hole-mediated double exchange through the strong p-d interaction between the Cu atom and neighboring N atom. The system of V_N defect in Cu-doped InN has the lowest formation energy. Due to the hybridization between the Cu-3d and V_N states, the spin-polarization on the Cu atoms in the InN lattice is reduced by V_N defect. So, it shows a weak ferromagnetic behavior.

Keywords : Cu-doped InN, first-principles, nitrogen defect, ferromagnetism

1. Introduction

Diluted magnetic semiconductor (DMS) materials have become a great interest because the charge from the s and p electrons of the semiconductor, and the spin from the magnetic dopant, can be used in spintronic devices. Group III-nitride semiconductors doped with 3d transition-metal (TM) such as Mn or Cr show the ferromagnetism with high Curie temperature, and it seems that their band structures are suitable for the spin-injection [1-4]. For instance, recent experimental work has been reported that the Cr-doped InN shows long range magnetic order above room temperature [5]. For the 3d TM-doped InN, it is greatly interested in their potential applications as spintronic devices within room-temperature ferromagnetism. But, it is one of the primary challenges to create the ferromagnetic semi-conductor due to the difficulty in the spin-injection into the semiconductors to form DMSs at room temperature or above room temperature. It may depend on some initial conditions in the process of the growth of single crystal. As it is well known, InN has direct energy band gaps of about 0.7-1.0 eV [6-11] or about 1.9 eV [12].

We have studied by using first-principle calculations for the magnetism of Cu as nonmagnetic dopant to fabricate InN-based DMS. We have presented the results for the band structure and magnetic moments under various doping concentrations with (or without) defects of nitrogen, and also calculated equilibrium lattice parameters by considering the stability of wurtzite structure. The defects of nitrogen and the dopants in group III-nitride semiconductors are believed to play important roles in the band-structure of DMSs. Recently, other theoretical studies [13, 14] have been confirmed that the nitrogen vacancy should be the dominant defect in GaN with introducing of the defect state through the Fermi level. Thus we have focused on the magnetism and the effects of N vacancy on electronic properties in Cu-doped InN with the Cu concentration in ranges from 2.77 to 8.33%. We have also considered the lattice distortion through the relaxation of atomic coordinate on the Cu sites.

2. Theoretical Approach

The electronic structure and magnetic properties on the Cu-doped InN at a concentration of 2.77%, 5.55%, and 8.33% have been investigated for a supercell of 72 atoms by replacing one, two, and three In atoms by Cu atom. All calculations were done using a full-potential linear muffin-tin orbital (FPLMTO) method [15] based on spin density functional theory within the generalized gradient approximation (GGA) [16] with the exchange-correlation function proposed by Janak-Moruzzi-Williams scheme

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[17]. The valence electrons were not assumed to have the spin-orbit coupling but had generated the self-consistent supercell potential by considering the scalar relativistic effects. The atomic potentials were approximated by spherically symmetric potential, however the full charge density including all non-spherical terms was evaluated by the Fourier transformation in the interstitial region.

Brillouin zone integrations were performed with the special k-point method over a gamma-centered $4 \times 4 \times 4$ mesh. The special points of $4 \times 4 \times 4$ mesh were corresponding to 64 k points. Using these k points insured that the total energies and the magnetic moments were converged on a better 1.0 meV/cell and 0.01 μ_B/atom, respectively. The LMTO basis set and charge density were expanded in terms of the spherical harmonics up to $l = 6$ inside each muffin-tin sphere. The LMTO basis functions in the valence energy region were chosen as 5s, 5p and 4d for In, and 4s and 3d for Cu. The basis function of In (or N) for the 5s (or 2s), 5p (or 2p), and 4d is generated with cut-off energy of 156.40 eV (or 439.28), 227.12 eV (or 640.56), and 330.48 eV, respectively.

3. Results and Discussion

The calculated equilibrium lattice parameters are $a = 3.480$ Å, $c = 5.615$ Å, and internal parameter $u = 0.3808$ for the clean InN. For the Cu concentrations of 2.77% and 5.55%, the equilibrium lattice parameters were contracted
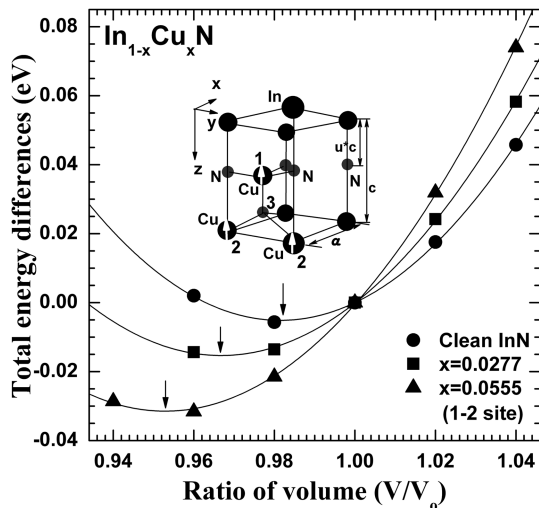

Fig. 1. Total energy difference of supercell containing 2.77% and 5.55% Cu in the perfect InN as a function of the ratio of unit-cell volume (V_o). V_o is 31.097 Å in the experiment [18]. Arrows denote the positions of minimum. Wurtzite unitcell is shown in the inset. Number 1 and 2 denote the substituted Cu atoms (ferromagnetic configuration), number 3 denotes the N or V_N site.

by a 1.6% and 2.9%, respectively, as compared to that of clean InN. The calculated parameters for clean wurtzite InN, are in agreement with the experimental ones [18, 19]. These results are shown in Fig. 1. The supercells of two Cu atoms positioned along the c-axis and of those in the xy-plane are referred to as '1-2 site' and '2-2 site' configurations, respectively. The Cu orders ferromagnetically in InN. It is energetically more favorable than the nonmagnetic (NM) or antiferromagnetic (AFM) states. The difference in total energies between the ferromagnetic (FM) and NM (or AFM) states is 45 meV (or 41 meV) in the concentration of 2.77%. Even though it increases up to a Cu concentration of 8.33%, the Cu dopant is maintained to the FM state.

We considered that two Cu atoms in InN are distributed with the nearest neighboring sites of '2-2 site' and '1-2 site' configurations. The calculated band gap of clean wurtzite InN is 0.7 eV. This value is close to the experimental one [9, 10]. In general, the value of band gap calculated using the first-principles GGA is less than that obtained in the experiment. When the vacancy of nitrogen (V_N) is considered, it occur the valence-band resonance by Cu, the perturbation of valence band by V_N can be observed in InN bands. It occur the downward shift in energy by 1.5 eV in comparison with complete un-doped InN. The V_N state lies mainly on the Fermi level (E_F), and lie at the bottom of conduction band and the top of valence band. These states make a result of strong hybridization between N-2p band, Cu t_2 (or d_{xy}) band, and Cu e (or d_{x2-y2}) band. Hence, the Cu magnetic moment is reduced to 0.19 μ_B from the value of 0.57 μ_B for Cu-doped InN without the V_N. The partially filled Cu e-band lies just below the top of the valence band, while the t_2-band falls into the valence band by (E_F -1.9) eV.

For a 5.55% Cu, it shows that '2-2 site' system is energetically more favorable than '1-2 site' system. The difference in the total energy between the '2-2 site' and '1-2 site' systems is a -0.208 eV. While for the concentration of 8.33%, the '1-2 site' is more favorable. Its difference is +0.029 eV. These results are listed in Table 1. In the case of '1-2 site' configuration, when the concentration of Cu dopant increases, the Cu magnetic moment is decreased. While for '2-2 site' configuration it is increased from 5.55% to 8.33%. However, the '2-2 site' system of 8.33% Cu concentration is not energetically favorable state. According to the Cu concentration increases, the magnetic moment becomes very small. In comparison with recent other theoretical works, it has been reported that the Cu-doped ZnO has the FM ground-states at the concentration 2.77% and 5.55% [20]. It shows that the Cu magnetic moment is 1.0 μ_B per Cu atom

Table 1. The difference in total energy (DE) for '2-2 site' and '1-2 site' configurations, vacancy formation energies (E_{fm}), substitution (E_{ss}) energies (in eV), and magnetic moments (in μ_B) of Cu and N (the nearest neighboring atoms from Cu) atoms for the $In_{1-x}Cu_xN$. The N magnetic moment is average value of the nearest neighboring N atoms from the Cu site(s). Formation energy is defined as $E_{tot}(In,N) - E_{tot}(In,N,V_N) - E_{tot}(N)$. Substitution energy is defined as $E_{tot}(In,N,[V_N]) - E_{tot}(In)) - E_{tot}(In,Cu,N,[V_N]) - E_{tot}(Cu))$, where $E_{tot}(In,N,[V_N])$ is the total energy of undoped-InN with (or without) the V_N, $E_{tot}(In,Cu,N,[V_N])$ is the total energy of Cu-doped system with (or without) the V_N. $E_{tot}(In,N)$ is the total energy of perfect InN without the V_N site, $E_{tot}(In)$, $E_{tot}(Cu)$, and $E_{tot}(N)$ are that of an isolated In, Cu and N atoms. The s_{22} and s_{12} represent the Cu sites of '2-2 site' and '1-2 site' configurations, respectively.

Cu site	Configurations	ΔE (eV)	E_{fm} E_{ss}	Magnetic total/cell	moment Cu	N
	$InN+V_N$	-	-6.581	-	-	-
	$In_{0.9723}Cu_{0.0277}N$	-	-1.954	1.55	0.57	0.21
s_{22}	$In_{0.9445}Cu_{0.0555}N$	-0.208	-1.804	0.02	0.01/0.01	0.00
s_{12}		0.0	-1.838	0.55	0.14/0.12	0.04
s_{22}	$In_{0.9167}Cu_{0.0833}N$	+0.029	-1.617	1.38	0.21/0.21/0.21	0.14
s_{12}		0.0	-1.608	0.51	0.08/0.08/0.08	0.04
	$In_{0.9723}Cu_{0.0277}N+V_N$	-	-0.557	0.38	0.19	0.05
s_{22}	$In_{0.9445}Cu_{0.0555}N+V_N$	+0.452	-1.064	0.48	0.16/0.10	0.04
s_{12}		0.0	-0.838	0.32	0.03/0.14	0.03

regardless of a Cu concentration.

The magnetic moment per Cu atom is a 0.57 μ_B at a low Cu concentration (2.77%). In comparison with the previous theoretical work [21], the Cu magnetic moment in GaN is 0.70 μ_B. The four surrounding N atoms in the CuN_4 tetrahedron are polarized with a magnetic moment of 0.20 μ_B for the top site N and 0.21 μ_B for the other three N in the basal plane. For 5.55% of Cu, the magnetic moments of two Cu atoms in '1-2 site' system are 0.12 μ_B and 0.14 μ_B, respectively. While that of two neighboring Cu atoms positioned to the '2-2 site' is about 0.02 μ_B. In the case of Cu concentration of 8.33%, the magnetic moments for the '1-2 site' and '2-2 site' Cu sites are 0.08 μ_B and 0.21 μ_B, respectively. Therefore, when the concentration increases without the V_N site, we can see that the Cu magnetic moment is decreased. For the Cu-doped InN with 2.77% without the V_N site, the charge configurations of Cu and N atoms are $4s^{0.49}4p^{0.92}3d^{9.24}$ and $2s^{1.2}2p^{3.5}$, respectively, within muffin-tin sphere. Since it occur the loss of the electrons on the Cu site, the charge moves into the interstitial and the V_N sites by 0.7e. When there is another Cu atom near one Cu atom, the charge configuration of N-2p electrons is not changed, while the electronic density of Cu-3d state on each Cu site changes a little (10.2e). Due to the strong hybridization between the N-2p and Cu-3d states, the spin-polarization of Cu-3d electrons is reduced. In Fig. 2, it can be seen that the E_F enters into the top of valence band in spin down channel, while spin up one exhibit semiconducting behaviors, suggesting half-metallic properties with 100% spin polarized current at the E_F. It is close to that of Cr-doped InN in the
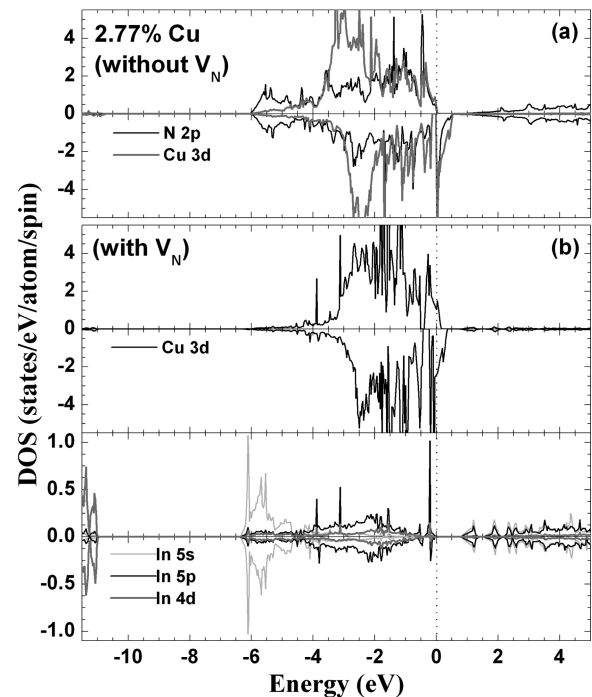

Fig. 2. (a) Partial spin DOS of N-2p and Cu-3d without the V_N, (b) partial spin DOS of Cu-3d with the V_N, and partial DOS of In-5s, 5p, and 4d with the V_N in $In_{0.9723}Cu_{0.0277}N$. The E_F (dotted line) is set to zero.

other calculations [22]. The spin polarization mainly comes from the p-d hybridized states of N 2p and Cu 3d electrons, while N 2s and In 4d contribute relatively less.

When there is the V_N site, we focused on the electronic structure and ferromagnetic coupling-states of single or
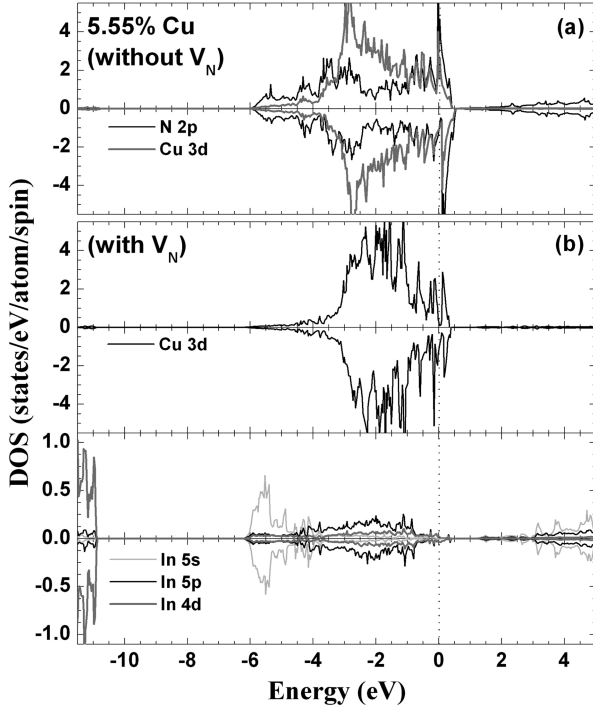
Fig. 3. (a) Partial spin DOS of N-2p and Cu-3d without the V_N, (b) partial spin DOS of Cu-3d with the V_N, and partial DOS of In-5s, 5p, and 4d with the V_N in $In_{0.9445}Cu_{0.0555}N$ of '1-2 site' Cu sites. The E_F (dotted line) is set to zero.

Fig. 4. Total energy change with respect to unrelaxed lattice, total magnetic moment per supercell as a function of the Cu-N-Cu angle in Cu-doped InN. The Cu concentration is 5.55%.

two Cu-doped InN. Fig. 3 shows the partial spin DOS of $In_{1-x}Cu_xN$ for $x = 0.0555$. At the top of the valence band, the hybridization between the Cu 3d and N 2p induces a metallic behavior. However, the spin splitting is very small, yielding to almost identical partial occupations of both spin-up and spin-down channels. For the Cu concentration of 2.77%, the magnetic moment of supercell in one Cu-doped InN with the V_N is approximately 35% amount of that without the V_N site. The crystal field splitting of e and t_2 bands within the V_N is larger than that of perfect Cu-doped InN. When the Cu concentration increases, the energy of crystal-field splitting between e and t_2 bands increases a little. It shows the downward shift in energy by the V_N site. The energy shift is 1.35 eV in comparison with clean InN. While for the Cu-doped InN with the V_N site, it shows the upward shift in energy. The charge of V_N site is polarized to opposite direction with that of neighboring Cu or N site.

As can be seen in the Fig. 2 or Fig. 3, the lowest conduction band and the highest valence band originate mainly from the N-2p and Cu-3d states. The Cu-3d states with the V_N site hybridize with the N-2p states in the top of valence band forming bonding states. The N-2s states locate around -11 ~ -15 eV. The N defect states, as the reduction of Cu magnetic moment, play important role in
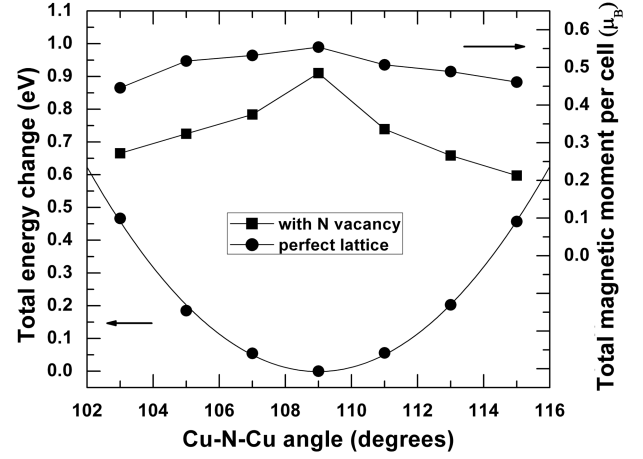
the dopant states around the E_F. We find that the Cu-3d states substantially hybridize with the V_N states. So, the Cu 3d-3d spin-coupling becomes very weak. The Cu magnetic moment is strongly reduced. We also considered the In vacancy as possible intrinsic defects. However, we find that the In vacancy does not seem to affect the weak FM behavior in Cu-doped InN. The FM coupling of Cu dopants is mediated by the bridging N atoms between two Cu sites as wave function between the N 2p and Cu 3d states overlap clearly in the spin-up and spin-down channels. The distance of two Cu (1-2 sites in Fig. 1) is too far to allow significant direct overlap of the unpaired electron wave functions. From these facts, we confirm a hole-induced double-exchange mechanism through the p-d indirect interaction via N atom.

Furthermore, we studied the ferromagnetism for a various positions of Cu sites. For each point in Fig. 4, the atomic coordinates of Cu dopants are allowed to vary. In order to verify whether the atomic relaxation is indeed responsible for diminishing or increasing the magnetic moments, we performed the calculations for various Cu-N-Cu angles. As a consequence of the relaxation of the Cu atoms, the magnetic moments on both Cu and N atoms change significantly. The atomic coordinates of two Cu sites (1 and 2 sites in the inset Fig. 1) were allowed to relax. So, the Cu-N-Cu angle and Cu-N bond length are different for each point, but the Cu-N bond length of 1-3 or 2-3 site does not variable. The Cu-N-Cu angle was varied between 103° and 115° (109° for unrelaxed lattice). Therefore, we note that it does not undergo a Jahn-Teller distortion by Cu dopant in the region around V_N defect in the wurtzite InN. The magnetic moment per cell is shown in Fig. 4.

Finally, the V_N site can be harmful to the ferromagnetism through destroying the FM coupling between two nearest neighboring Cu atoms. When the Cu doping concentration increases, the V_N site will be generated on the nearest neighboring Cu sites in order to reduce the total energy of the system (*i.e.* N-poor environment). Thus the Cu dopant will combine with the N vacancy to form Cu+V_N state. At this point, it is noticeable that the N partial pressure should be enhanced to reduce the appearance of V_N, avoiding the destruction of FM coupling of the Cu atom by the V_N site.

4. Conclusion

The defect and dopants are believed to play important roles in the band-structure of DMSs. Thus we have aimed the investigation for the electronic structures and magnetism under various doping concentrations with (or without) the V_N using detailed first-principles calculations. We have considered N vacancy and some relaxation of Cu dopants as possible intrinsic defects and distortions in the wurtzite InN. We have reported that the electronic structures are strongly correlated by the defect of N or Cu dopant in InN. The Cu magnetic moment is strongly reduced due to the hybridization between the Cu-3d and the V_N bands. The formation of Cu-Cu in InN with the V_N site is energetically more favorable than that without the V_N site. When the number of Cu atoms occupying adjacent cation lattice position increase, the Cu dopant will combine with the V_N site easily, such as to form Cu+V_N state. It is noticeable that the observed FM behavior might be dependent on the V_N concentration and open therefore the possibility for further investigations. The In vacancies do not affect the weak FM behavior in Cu-doped InN, while the introduction of N vacancies leads to a lack of ferromagnetism. Thus robust ferromagnetism of Cu-doped InN is weak. The observed long-range FM order can be attributed to the hole-mediated double exchange through the strong p-d interaction between the Cu atom and neighboring N atom. These results suggest a recipe tuning the ferromagnetism of spintronic materials by controlling the intrinsic defects. We have confident that our results can answer some questions concerning lattice relaxation and the influence of native defects in Cu-doped InN.

Acknowledgment

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