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Electronic Structure and Magnetic Moments of Copper-atom in/on GaN Semiconductor

Byung-Sub Kang[1]* and Haeng-Ki Lee[2]

[1]*BK 21 Physics program and Department of Physics, Chungbuk National University, Cheongju 361-763, Korea*
[2]*Department of Radiotechnology, Daegu Polytechnic College, Daegu 706-711, Korea*

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The electronic and magnetic properties of Cu-doped GaN with a Cu concentration of 6.25% and 12.5% are examined theoretically using the full-potential linear muffin-tin orbital method. The magnetic moment of Cu atoms decreases with increasing Cu concentration. The spin-polarization of Cu atoms is reduced due to the Cu d-d interaction depending on the distance between the nearest neighbouring Cu atoms. Cu atoms exhibits a clustering tendency in GaN. For Cu-adsorbed GaN thin films with a surface coverage of 0.25, the ferromagnetic state is found to be the energetically favourable state with an induced magnetic moment of 0.54 μ_B per supercell.

Keywords : nonmagnetic dopant, ferromagnetic ordering, thin film

1. Introduction

Group III-nitrides with magnetic dopants [1-9], such as 3d transition-metals of V, Cr, Mn, Fe, Co, and Ni, have attracted considerable interest due to their potential applications in spintronics devices that utilize both the charge and spin of electrons to create new functionalities beyond conventional semiconductors. Ideal diluted magnetic semiconductors (DMSs) should exhibit ferromagnetism at room temperature for practical applications and have a homogeneous distribution of magnetic dopants. However, the presence of magnetic precipitates in the host semiconductor in forms of clusters or secondary phases of magnetic impurities is detrimental to their real applications. For example, in Mn-doped GaN, clusters of Mn and secondary Ga-Mn and Mn-N phases have been observed [10, 11]. In Cr-doped GaN, the magnetic moment of Cr in GaN was significantly smaller than the expected saturation value by 3 μ_B, and varied in a wide range by 0.2-1.8 μ_B per atom [12-14].

The precipitates of nonmagnetic (NM) dopants do not contribute to the magnetic ordering. Recent theoretical investigations have reported the ferromagnetic ordering of normally NM materials in GaN [15-18]. For 4*d*-metal Pd in GaN, Pd orders ferromagnetically in GaN [15]. Clusters of Pd were found experimentally to be ordered ferromagnetically. Taniyama *et al.* reported that the magnetization of Pd increases rapidly with decreasing Pd particle size [19]. Cox *et al.* [20] have reported that Pd clusters with more than 12 atoms exhibit NM ordering. This shows that the magnetic moment is sizable with a small particle size < 10 atoms. The size of a cluster has an effect on the spin-polarization of Pd atoms. Besides Pd, it has been predicted that a 3*d*-metal Cu is a potential NM dopant for GaN, even though more challenging theoretical and experimental investigations are needed. Wu *et al.* [16] reported that Cu-doped GaN with 6.25% favors a ferromagnetic ground state. They showed that the spin-polarization of Cu and the neighboring N atoms can be explained in terms of *p-d* hybridization. In the case of Cu-doped ZnO, Ye *et al.* examined ferromagnetism by numerical calculations based on density functional theory [21]. They also predicted that the electronic states near the Fermi level form strong hybridization between the Cu dopant and neighboring O atoms. Interestingly, the local magnetic moment of Cu atoms is not dependent on the Cu concentration. However, for Cu-doped ZnO thin films, the local magnetic moment decreased with increasing Cu concentration [22]. In this study, the possibility of Cu as a NM dopant to fabricate GaN-based DMS is evaluated by first-principles calculations based on spin density functional

*Corresponding author: Tel: +82-43-261-3338
Fax: +82-43-274-7811, e-mail: kangsub@cbnu.ac.kr

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theory with the main focus on the spin-polarization of Cu and neighboring N atoms with increasing Cu concentration. In contrast to Cu-doped ZnO [21], the spin-polarization of the Cu dopant in GaN decreases with increasing Cu concentration. The Cu dopant in GaN may form clusters or secondary Ga-Cu or Cu-N phases. As mentioned above, these precipitates do not contribute to the magnetism.

2. Modeling and Calculations

The electronic properties on Cu-doped GaN at a concentration of 6.25 and 12.5% are investigated for supercells containing 32 atoms with one and two Ga atoms substituted by Cu. Supercells of 72 atoms with one, two, three and four Ga atoms substituted by Cu are also examined, i.e. four doping levels are checked. In addition, a calculation of a thin film adsorbed Cu in the surface layer (by substitution) is performed. The electronic properties of the thin film are compared with those of $Ga_{1-x}Cu_xN$ (x=0.0625 and 0.125), where applicable in our considered supercell. The wurtzite GaN substrate (thin film) is modeled by eight atomic layers, which are separated by six layers of vacuum. The atomic structure with one Ga atom substituted with Cu corresponds to a surface coverage of 0.25.

The experimentally determined lattice constants of GaN in the wurtzite structure are used in the calculations, with a=3.162 Å, c=5.142 Å, and u=0.377 [23], where u is the displacement of Ga and N sublattices along the c axis. That is, the nearest neighboring distance is 0.377c (=u*c). The c/a ratio of GaN is slightly larger than that reported previously [23]. The equilibrium lattice structure is expanded by 0.6% compared to the experimental one. The equilibrium lattice constants a and c of wurtzite GaN are 3.1809 and 5.1728 Å, respectively. This study is performed using the first-principles full-potential linear muffin-tin orbital (FPLMTO) method [24, 25] within both the local density approximation (LDA) and generalized gradient approximation (GGA) with the exchange-correlation functional proposed by the Janak-Moruzzi-Williams scheme [26]. The electron wave function is expanded in plane waves with a cut-off energy of 252.96 (224.40), 368.56 and 539.92 (477.36) eV for the s, p, and d orbitals of Ga (Cu), respectively. The charge density is determined self-consistently using gamma-centered 4×4×4 and 6×6×2 grids, respectively, in the Brillouin zone for the bulk and thin film systems, which corresponds to 64 and 72 k points, respectively. Using the number of k points ensures that the total energies and magnetic moments are converged within 10 meV/cell and 0.01 μ_B/atom, respectively.

3. Results and Discussion

The ferromagnetic (FM) order of Cu atoms in GaN is more energetically favorable than theNM or antiferromagnetic (AFM) states. The ferromagnetic state is more energetically favorable than the AFM state, and its difference in energy is quite small (31.5 meV) for a concentration of 6.25%. The differences in the total energies between the FM and NM states at 6.25 and 12.5% Cu are 73.5 and 108.8 meV, respectively. The magnetic energy gain in high concentrations is larger than that at lower concentrations. For a Cu concentration of 6.25%, the equilibrium lattice constants changed slightly by 0.1%, −0.003 Å for a and −0.005 Å for c after structural optimization. For a Cu concentration of 12.5%, the equilibrium lattice constants changed by −0.011 Å and −0.015 Å for a and c, respectively, compared to pure GaN. For pure GaN, the LDA calculation provides similar results to the experimental results (~22.3 $Å^3$ in the unit-cell volume). However, shows the GGA overestimates the calculated equilibrium unit-cell volume with a 23.8 $Å^3$ (Fig. 1). The volume of a supercell decreases with increasing Cu concentration. These decreases are attributed to the small difference in atomic radius between Cu and Ga. Each Cu-N bond length of the CuN_4 tetrahedron is approximately 2.024 Å with some structural distortion present. In the case of two Cu atoms, two cases of the Cu-Cu distance with the tetrahedral structure are considered. That is, the Cu-Cu distance is 3.1585 and 3.1778 Å for two Cu atoms positioned along the c-axis and in a basal plane, respectively. The system with a Cu-Cu distance of 3.1585 Å in GaN is more energetically favorable than that of 3.1778 Å. The difference in the total energies between both systems with a Cu-Cu distance of 3.1585 and 3.1778 Å is 346 meV per supercell. Therefore, there is a tendency for Cu clustering

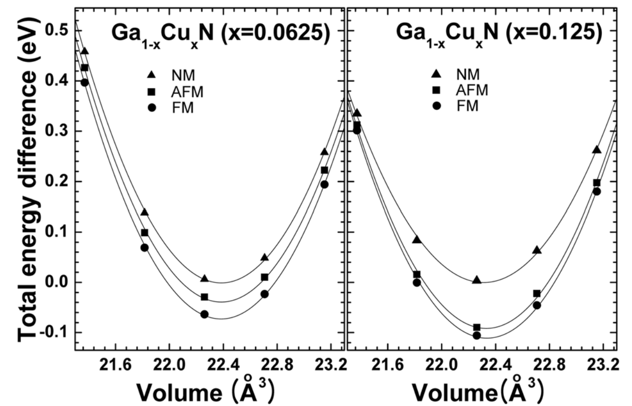

Fig. 1. Total energy differences of the super cell containing 6.25% and 12.5% Cu with respect to the reference NM state as a function of the unit-cell volume ($Å^3$).

Table 1. Magnetic moments (μ_B) and band-splitting energies of impurity atoms (ΔE, eV) for a thin film with a surface coverage (θ) of 0.25 and $Ga_{1-x}Cu_xN$. Cu1 or Cu2 denotes the occupied Cu site. The results are compared with those of other previous calculations (parenthesis).

Magnetism	Thin film Surface FM	Two doping level		
		Cu1	Cu1	Cu2
		FM/AFM	FM/AFM	FM/AFM
Cu	0.27	0.67 (0.70)[a]/0.54	0.06/0.21	0.13/0.27
N (in CuN_4)	(θ = 0.25)	(x = 0.0625)	(x = 0.125)	
Top site	–	0.18 (0.22)[a]/0.12	0.02/0.03	0.03/0.03
Basal site	0.09	0.20 (0.25)[a]/0.14	0.03/0.06	0.04/0.07
ΔE	0.301	0.731/0.639	0.068/0.238	0.108/0.234

[a] Ref. [7]

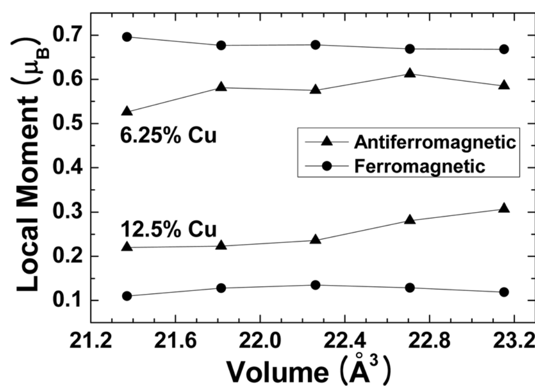

Fig. 2. The magnetic moment of Cu atoms in Cu-doped GaN containing 6.25% and 12.5% Cu as a function of the unit-cell volume (Å^3).

in Cu-doped GaN. A Cu-Cu distance of 3.1778 Å corresponds to a lattice parameter of a. This is slightly different from the electronic structure each other. In Table 1, the two sites are represented as Cu1 or Cu2 (see Fig. 3). The four N sites and Cu1 or Cu2 site have the structure of a distorted CuN_4 tetrahedron. The magnetic moments of these sites are listed in Table 1, and are compared with those of the thin film.

For the Cu concentration of 6.25% with the FM state, the Cu atom is found to be the main contributor to the magnetic moment with a localized magnetic moment of 0.67 μ_B per atom. The four surrounding N atoms in the CuN_4 tetrahedron are polarized with a magnetic moment of 0.18 μ_B for the top N site and 0.20 μ_B for the other three N sites in the basal plane. The smaller magnetic moment for the top site N is due to a distortion of the tetrahedron, i.e. the Cu-N bond is smaller for the top site N than the three lying in the basal plane. This is also because the spin-polarization of the Ga and other N atoms away from the CuN_4 tetrahedron is very small. At a concentration of 12.5%, the total magnetic moment per supercell in the ground state is 0.48 μ_B, or 0.06 μ_B or 0.13 μ_B per Cu atom. The nearest neighboring four N atoms are polarized with average magnetic moments of 0.03 μ_B per N atom. The FM state is more energetically favorable than the other states. The local magnetic moment for the FM state is almost constant regardless of the lattice parameter, whereas it increases slightly for the AFM state, as shown in Fig. 2. The spin-polarization of the supercell decreases with increasing Cu concentration. This is due to $3d$-$3d$ hybridization by the Cu-Cu interaction depending on the distance between the nearest-neighbor Cu atoms. At low dopant concentrations, the Cu magnetic moment of the FM state is larger than that of AFM state. On the other hand, for a high concentration, the Cu magnetic moment of the AFM state is slightly larger than that of the FM state. The magnetic property of Cu in GaN depends on the dopant concentration. The magnetic moment of Cu atom decreases with increasing concentration.

The calculations are repeated using a supercell with one, two, three and four substitutional Cu atoms, which corresponds to a concentration of 2.78, 5.55, 8.33 and 11.11%, respectively. In the case of 5.55% Cu, the supercell consists of 72 atoms with two Ga atom substituted by Cu. The electronic and magnetic properties of the super-

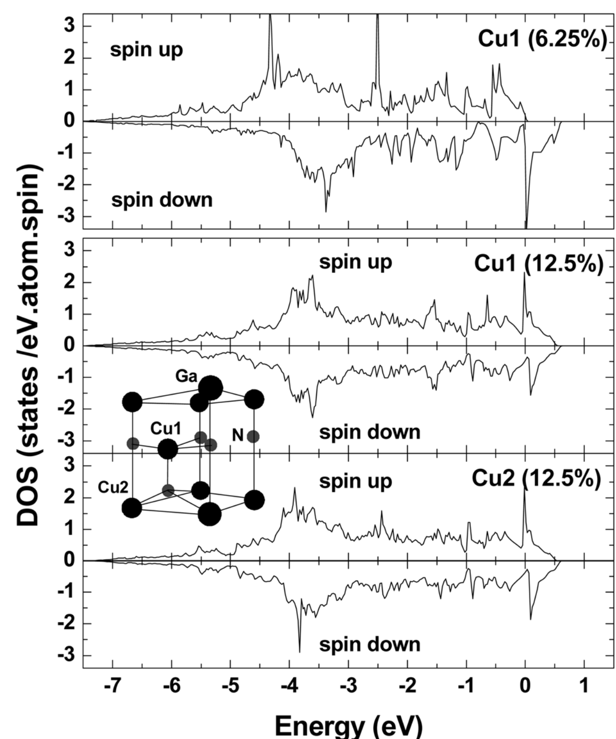

Fig. 3. Projected DOS for Cu in $Ga_{0.9375}Cu_{0.0625}N$ and $Ga_{0.875}Cu_{0.125}N$. The Fermi level is set to zero. The atomic sites of Cu1 and Cu2 are shown in the inset.

cell are similar to those of the system consisting of 32 atoms with one Ga atom substituted by Cu. For the equilibrium atomic volume of these calculations, all NM and FM phases range from 21.37 to 23.15 Å^3, corresponding to an equilibrium Wigner-Seitz radius $r_{WS} \sim$ 2.69 a.u..

The electronic configuration of Cu and N atoms is $4s^{0.42}4p^{0.42}3d^{9.00}$ and $2s^{1.11}2p^{2.26}$ within the muffin tin sphere, respectively. A charge of 1.16*e* (1.63*e*) per Cu (N) site moves into the interstitial region. The charge configuration of N p electrons is not changed when there is another Cu atom near a Cu atom, whereas the electronic density of the 3d state in each Cu site changes slightly due to the Cu-Cu interaction and difference in the nearest neighboring Cu-N distance. The charge configuration changes to a repulsive interaction between Cu 3d and N 2p electrons. Accordingly, the spin-polarization of Cu 3d electrons is reduced. The magnetic moment of Cu atoms should decrease with increasing Cu concentration.

Fig. 3 shows the projected densities of states (DOS) for $Ga_{0.9375}Cu_{0.0625}N$ and $Ga_{0.875}Cu_{0.125}N$. The introduction of

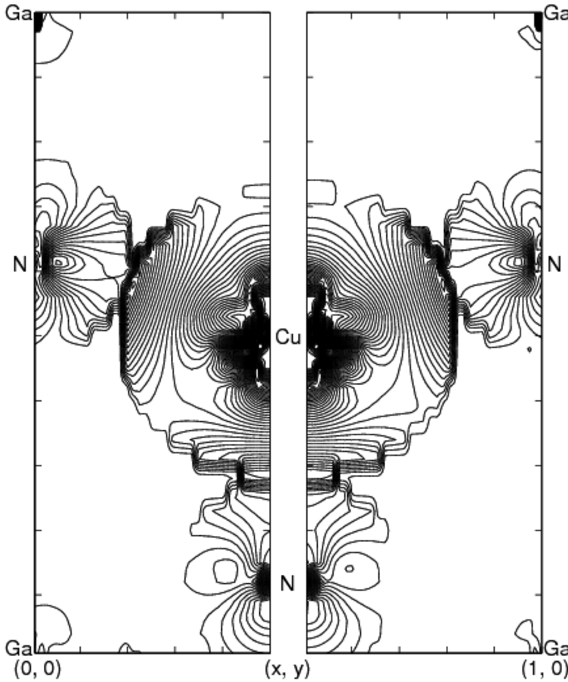

Fig. 4. The charge density difference ($\Delta\rho(r,R)$) for $Ga_{0.9375}Cu_{0.0625}N$ in the ground state. $\Delta\rho(r,R)$ is defined as $\rho^{Cu}_{GaN}(r,R)-\rho_{GaN}(r,R)-\rho^{Cu}(r,R)$, where $\rho^{Cu}_{GaN}(r,R)$ is the total charge density, $\rho_{GaN}(r,R)$ and $\rho^{Cu}(r,R)$ are the charge densities for GaN with a empty site (point defect of Ga site) and isolated one Cu atom, respectively. The contour is shown on the plane of $(11\underline{2}0)$ with intervals a 2.0×10^{-4} $e/(\text{a.u.})^3$. The coordinate of (x,y) corresponds to $(1/2, \sqrt{3}/6)$. Here, the lattice parameter of *a* is set to 1.

Cu in GaN shows a slight upward shift in energy by 0.35 eV up to the Fermi level (majority-band). The electrons of the dopant are spin-polarized with a splitting-energy of 0.731 eV per Cu atom. The unoccupied minority-band maximum is located at approximately 1 eV. The Cu band is formed by the Cu 3d level hybridizing with the 2p levels of the N neighbors of Cu. In the case of a thin film, the number of neighboring N atoms on the surface Cu site is lower than that of Cu-doped GaN. Therefore, the interaction between the Cu 4d and N 2p states is weak. The energies of spin-splitting between their atoms are low and the spin-polarization is reduced. The band gap of pure GaN thin film is narrowed by the surface states. The Cu magnetic moment is decreased by 0.27 μ_B per Cu atom. This result is compared with previous work [27]. This is a similar trend to that of Cu-doped ZnO thin films with magnetic moment of 0.4 μ_B per Cu atom [22].

Fig. 4 shows the charge density of $Ga_{0.9375}Cu_{0.0625}N$ within the FM state, and can be compared with the interaction between Ga, Cu, and N atoms. A strong Cu-N interaction occurs by large charge accumulation between neighboring Cu and N atoms. The cohesive energy of one Cu atom in GaN is −8.99 eV. The cohesive energy is defined as follows: $E_{tot}(Ga,Cu,N)-E_{tot}(Ga,N)-E_{tot}(Cu)$, where $E_{tot}(Ga,Cu,N)$ is the total energy of Cu-doped system, $E_{tot}(Ga,N)$ is the total energy of pure GaN, and $E_{tot}(Cu)$ is that of an isolated Cu atom. The exchange splitting-energy between the spin-down and up bands of Cu 4*s* and 3*d* are 0.408 eV and 0.323 eV, respectively. The N magnetic moments by an interaction of Cu-N atoms are sizable. The peak at −4.36 eV of Cu-3*d* in the majority spin-channel overlaps that of N-2*p* at the CuN_4 tetrahedron. The peak at −0.56 eV of Cu-3*d* also overlaps with that of N-2*p*. In the minority spin-channel, the 2*p* state of the four connecting N atoms contributes significantly to the unoccupied states. These characteristics indicate strong hybridization between Cu and its four neighboring N atoms. The Cu atom hybridizes strongly with the neighboring anions of GaN. Thus, the neighboring anions are spin-polarized with large (relatively) magnetization in the same order as that of the dopant. The Cu-N interaction has a strong effect on N magnetization by the presence of Cu neighbors with a low concentration. However, the Cu local moment should disappear as the Cu concentration increases.

4. Conclusions

This study examined the electronic and magnetic properties derived from the band structure calculations for a thin film and Cu-doped wurtzite GaN using the FPLMTO

method. The NM dopant at low concentrations becomes spin-polarized when incorporated substitutionally into GaN. The FM state is more energetically favorable than the AFM or NM states. FM ordering of the dopant and four neighboring N atoms is produced by strong *p-d* hybridization. However, the magnetic moment per Cu atom decreases with increasing Cu-doping concentration. The reduced magnetic moment is due to an increase in the number of Cu atoms occupying the adjacent cation lattice positions.

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