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First-principles Study on Magnetism of Cu in GaN

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The electronic properties of Cu or Pd-doped GaN at several concentrations are examined using the full-potential linear muffin-tin orbital method. For $(Cu_{0.055}Ga_{0.945})N$, the model reveals a magnetic moment of 1.47μB per supercell. The range of concentrations that are spin-polarized should be restricted within narrow limits. A paramagnetic to ferromagnetic phase transition is found to occur at a Cu concentration of 5.55%.

Keywords : Cu dopant, ferromagnetic ordering

1. Introduction

Magnetic dopants in host compound semiconductors, such as 3d transition-metals (V, Cr, Mn, Fe, Co, and Ni), have attracted considerable attention due to their potential applications in spintronics devices that employ both the charge and spin of electrons to create new functionalities beyond conventional semiconductors. However, the presence of magnetic precipitates in the host semiconductors in the form of clusters or secondary phases of magnetic impurities is detrimental to real applications. In Mn-doped GaN, clusters of Mn as well as secondary Ga-Mn and Mn-N phases have been observed [1, 2]. In Cr-doped GaN, the magnetic moment of the Cr dopant in GaN is significantly smaller than the expected saturation value of $3\mu_B$, and varied over a wide range of 0.2-1.8μ_B per atom [3-5].

Recent theoretical investigations have reported the ferromagnetic ordering of normally nonmagnetic (NM) materials in GaN [6-9]. The precipitates of NM dopants do not contribute to ferromagnetism. For 4*d*-metal Pd in GaN, it has been reported that the Pd orders ferromagnetically in GaN [6]. Clusters of Pd have been found experimentally to be ordered ferromagnetically. Taniyama *et al.* has reported that the magnetization of Pd increases rapidly with decreasing particle size of Pd [10]. Cox *et al.* [11] has reported that the Pd clusters from 12 to more than 100 atoms are NM ordering. The results show that the magnetic moment is sizable in small particles ranging in size from 1 to 10 atoms. The size of a cluster affects the spin-polarization of Pd atoms. In addition to Pd, 3*d*-metal Cu has been predicted to be a potential NM dopant for GaN, even though it requires more theoretical and experimental investigations. Wu *et al.* [7] has reported that GaN doped with 6.25% Cu favors a ferromagnetic ground state. They show that the spin-polarization of Cu and neighboring N atoms can be explained in terms of *p-d* hybridization.

2. Computational Method

The NM dopant of Cu(or Pd) in GaN can form clusters or the secondary Ga-Cu(or Pd) or Cu(or Pd)-N phase. These precipitates do not contribute to the magnetism. In the present study, the electronic properties of GaN doped with 5.55% Cu (or Pd) are studied for a supercell of 72 atoms with two Ga atoms substituted with Cu (or Pd). The experimentally determined lattice constants of GaN in the wurtzite structure were used in the calculations [12] (a=3.162 Å, c=5.142 Å, and u=0.377). The c/a ratio of GaN is slightly larger. The equilibrium lattice structure is expanded by 0.8% compared to the experimental one. The local spin-density approximation (LSDA) calculation gives a similar result to the experimental data. However, the generalized gradient approximation (GGA) increased the calculated equilibrium volume (see Fig. 1). This study is performed using the first-principles full-potential linear muffin-tin orbital (FPLMTO) method [14, 15] within both the LSDA with the exchange-correlation functional proposed by Wang and Perdew [16] and the GGA implemented in the Perdew-Burke-Ernzerhof scheme [17]. The

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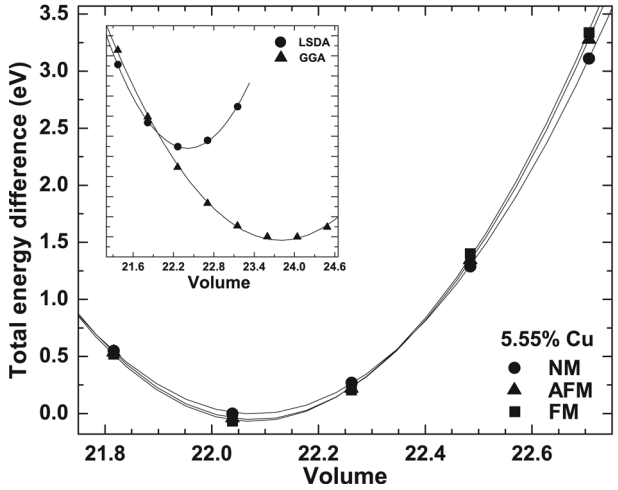

Fig. 1. Total energy difference at a concentration of 5.55% with respect to the reference of the NM state as a function of the unit-cell volume (Å^3). The differences in total energies for LSDA and GGA with clean GaN are shown in the inset.

electron wave function is expanded in plane waves with a cut-off energy of 252.96 (224.40), 368.56 or 539.92 (477.36) eV for the *s*, *p* or *d* of Ga (Cu), respectively. The charge density is determined self-consistently using a gamma-centered 4×4×4 *k* (corresponding to 64 *k* points) mesh in the Brillouin zone, which ensures that the total energy and magnetic moment converge to better than 1 meV/cell and 0.02μ_B/atom, respectively.

3.Results and Discussion

The electronic and magnetic properties of a supercell consisting of 72 atoms with two Ga atom substituted by Cu are similar to that of the system consisting of 32 atoms with one Ga atom substituted with Cu. The single Cu atom and nearest neighboring four N atoms forms a CuN_4 tetrahedron. Cu orders ferromagnetically in GaN, and is more energetically favorable than the NM and antiferromagnetic (AFM) states. The ferromagnetic (FM) state is more energetically favorable state than the AFM state on the *xy* plane (or basal plane), and its difference in energy is quite small. The difference in total energy between the FM and NM states is 61 meV. The Cu atom is found to be the main contributor to the magnetic moment with a localized magnetic moment of 0.67μ_B per atom. The N magnetic moment of CuN_4 makes a small contribution of 0.20μ_B per atom. It is similar to that of the four N neighbors of Cu. These results are shown in Fig. 1 and Table 1. In Table 1, the results are compared with those from the 32 atoms system, which corresponds to a concentration of 6.25% [6, 7]. The calculated lattice constants of wurtzite GaN are a=3.187 and c=5.183 Å, which are

Table 1. Magnetic moments (μ_B) and band-splitting energies of the impurity atoms (ΔE, eV) for Cu(or Pd)-doped GaN. M_I and M_N denote the magnetic moments of the dopant and nearest neighboring N atoms, respectively. These results are compared with those of previous calculations (parenthesis).

	(Ga,Cu)N	(Ga,Pd)N
M_I	0.67 (0.70)[a]	0.57 (0.57)[b]
M_N	0.20/0.20	0.14/0.06
	(0.22/0.25)[a]	(0.15/0.18)[b]
ΔE	0.719	0.485

[a] Ref. [7], [b] Ref. [6]

in agreement with the experimental data. The equilibrium lattice constants changes slightly, –0.051 Å for a and –0.082 Å for *c*, after structural optimization. This reduction is a result of 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, and there is some structural distortion. In the case of the two Cu atoms, two different Cu-Cu distances with a tetrahedral structure are considered: 3.1585 and 3.1778 Å for two Cu atoms positioned along the c-axis and in the basal plane, respectively. The Cu-Cu distance of 3.1585 Å in GaN is more energetically favorable than 3.1778 Å. The difference in the total energy is 398 meV per supercell.

As shown in Fig. 1, a crossover of total energies is found. A paramagnetism (NM) to ferromagnetism phase transition occurs at this concentration. The calculations are repeated using a supercell with one, three and four substitutional Cu atoms, which corresponds to a concentration of 2.78, 8.33, and 11.11%, respectively. The lattice parameter of Cu-doped GaN changes with increasing Cu concentration. The distortion of the CuN_4 tetrahedra should increase with increasing number of Cu atoms occupying the adjacent cation lattice positions, or the local magnetic moment of the Cu atom should decrease. Therefore, the magnetic properties of Cu in GaN depend strongly on the dopant concentration. The equilibrium atomic volume of all NM and FM phases from these calculations ranges from 21.37 to 23.15 Å^3, corresponding to an equilibrium Wigner-Seitz radius of $r_{WS} \approx 2.69$ a.u.. In the cases of 8.33 and 11.11% Cu, it is not energetically favorable state to substitute Cu atoms in-plane (*xy* plane). This suggests that the Cu may prefer an inhomogeneous distribution in GaN.

Fig. 2 shows the projected densities of states (DOSs) of $(Cu_{0.055}Ga_{0.945})N$. The introduction of Cu to GaN shows a slight upward shift in energy (0.35 eV) to the Fermi level (majority-band). Therefore, the semiconducting nature of GaN deteriorates as a result of the introduction of Cu. The band of the dopant is spin-polarized with a splitting-energy of 0.72 eV. The maximum of the unoccupied

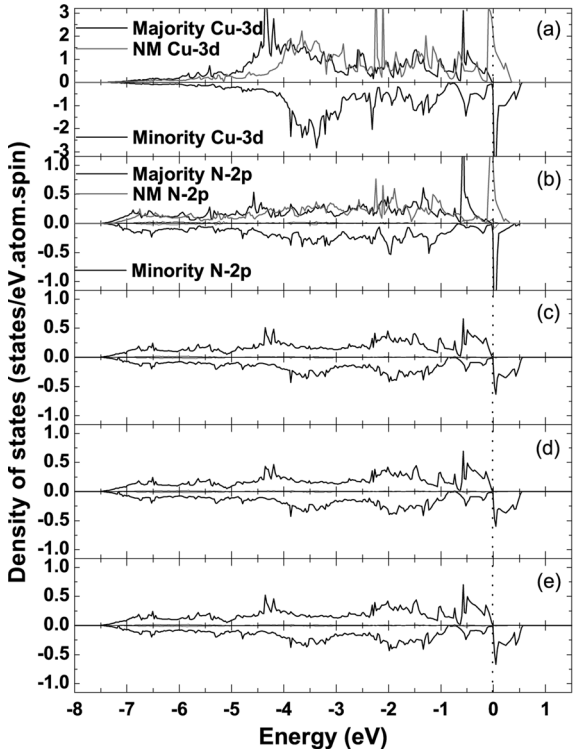

Fig. 2. Projected DOS for Cu-3*d* (a) and N-2*p* of the CuN_4 tetrahedron (b)-(e) within wurtzite $(Ga_{0.945}Cu_{0.055})N$. Gray solid-lines represent the NM state of Cu and the nearest neighboring N sites. The Fermi level is set to zero.

minority-band is located at approximately 1 eV. The Cu band is formed by the Cu 4*d* level hybridizing with the 2*p* levels of the N neighbors of Cu. The images in Fig. 2 illustrate the *p-d* hybridization. The Cu atom hybridizes strongly with it s neighboring anions of GaN. Therefore, the neighboring anions are spin-polarized with large (relatively) magnetization in the same order as that of the dopant. The state of the dopant is induced by the partially occupied bands in the GaN gap. The peak at –4.36 eV of Cu-3*d* in the majority spin-channel overlaps with 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.

4. Conclusions

This study examines the electronic and magnetic properties from the band structure calculations for Cu (or Pd)-doped wurtzite GaN using the FPLMTO method. The NM dopants become spin-polarized when incorporated substitutionally into GaN. FM ordering of the dopant and four neighboring N atoms is produced by the strong *p-d* hybridization. The range of concentrations that show a spin-polarized state should be restricted to within narrow limits. Although these systems are not represented in detail, the phase transition from the NM to FM state occurs at a concentration of 5.55%.

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