Magnetic properties of Ni doped gallium nitride with vacancy induced defect

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ABSTRACT

Investigations have been carried out to study the ferromagnetic properties of transition metal (TM) doped wurtzite GaN from first principle calculations using tight binding linear muffin-tin orbital (TBLMTO) method within the density functional theory. The present calculation reveals ferromagnetism in nickel doped GaN with a magnetic moment of $1.13\,\mu_B$ for 6.25% of Ni doping and $1.32\,\mu_B$ for 12.5% of nickel doping, there is a decrease of magnetic moment when two Ni atoms are bonded via nitrogen atom. The Ga vacancy (V_{Ga}) induced defect shows ferromagnetic state. Here the magnetic moment arises due to the tetrahedral bonding of three N atoms with the vacancy which is at a distance of 3.689 Å and the other N atom which is at a distance of 3.678 Å .On the other hand the defect induced by N vacancy (V_N) has no effect on magnetic moment and the system shows metallic character. When Ni is introduced into a Ga vacancy (V_{Ga}) site, charge transfer occur from the Ni 'd' like band to acceptor level of V_{Ga} and formed a strong Ni–N bond. In this Ni–V_{Ga} complex with an Ni ion and a Ga defect, the magnetic moment due to N atom is $0.299\,\mu_B$ .In case of Ni substitution in Ga site with N vacancy, the system is ferromagnetic with a magnetic moment of $1\,\mu_B$.

1. Introduction

Dilute magnetic semiconductor (DMS) materials are of intense interest because of the prospect of their application in the emerging field of spintronics. Furdyna [1] shows the exchange interaction between spin of s, p electrons of host with the d-electron of the doped transition metal ion is responsible for magnetic, optical and conductive properties of DMS materials. Dietl et al. [2] have proposed the possibility of ferromagnetism in GaMnN above room temperature based on first principle calculations. van Schilfgaarde and Mryasov[3] calculated energetics and magnetic properties from single to several number of Mn impurity in GaN and concluded that Mn related cluster is energically favorable and is responsible for the observed magnetism in the system. Sato et al. [4] proposed that ferromagnetism behavior is dominated by a short range double exchange mechanism in III–V compound semiconductors when transition metal forms a random alloy. Akinaga et al. [5] reported the ferromagnetic phase in (GaFe)N below 100 K. Rosa et al. [6] predicted weak ferromagnetism in Cu doped GaN and shows no effect on magnetization with the creation of Ga vacancy. Cui et al. [7] by using DFT theory shows that the Cr doping in GaN resulted in the formation of Cr cluster resulting antiferromagnetism. Wang et al. [8,9] have reported ferromagnetism in Cr doped GaN and the magnetic coupling mechanism is governed by double exchange. They have also reported that the magnetic coupling of Cr atom and their clusters formation is independent of whether the GaN is in thinfilm, nanowires or nanoholes form. Goumari et al. [10] doped Eu in GaN and find a high magnetic moment of $6\,\mu_B$. Jisang Hong [11] through the full potential linearized augmented plane wave method has explored the possibility of defect-induced magnetism in wurtize GaN. The N vacancy defect structure has no sign of a magnetic state. Nonetheless, very interestingly it has been found that the GaN with a Ga vacancy defect can show induced local magnetic moment in N atoms. The four N atoms in the tetrahedron sites with the Ga vacancy as neighbor have magnetic moments of 0.23 and $0.29\,\mu_B$ depending on their position in the vacancy induced defect by Ga in GaN. To our knowledge no theoretical calculation of Ni doped GaN have been reported. In this paper, we are presenting the result of our calculation of Ni doped GaN. It shows that Ni doped GaN is half metallic for 6.25% and 12.5% concentration. The defect created by Ga vacancy shows magnetic state whereas nitrogen vacancy has no role to play in magnetization. Ni substitution with Ga vacancy shows ferromagnetism which is due to the tetrahedral nitrogen bonding to V_{Ga} as indicated by Sanyal et al. [12] and Joongoo Kang [13]. They showed from their calculations that magnetization is much stronger for N when compared to Mn in Mn doped GaN. From the present study we also infer that Ni with V_N shows a magnetic moment of $1\,\mu_B$.

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2. Calculation method

The calculations are performed by means of TBLMTO method based on the density functional theory [14]. The local density approximation (LDA) parameterized by Barth and Hedin [15] was used for the exchange and correlation potential. GaN crystallize in the wurtzite structure with lattice constants $a=3.188$ Å and $c=5.189$ Å [16]. A periodic $2 \times 2 \times 2$ supercell of GaN with 64 atoms (32 real and 32 empty) was used as a calculation unit. Some defect such as Ga and N vacancies are considered in the supercell. Spin polarized scalar relativistic calculations are performed to obtain the total energy, density of states (DOS) and magnetic moment. In the irreducible part of the Brillouin Zone 144K points was used to calculate the total and partial density of states by means of tetrahedron method [17]. The K and E convergence are checked by increasing the number of K points and the energy convergence criteria.

3. Results and discussion

The schematic representations of unit cell for Wurtize GaN with vacancies used in our calculation are presented in Fig. 1. Ga, N, Ga vacancy, N vacancy and Ni are represented by violet, gray, yellow, blue and light green balls. One and two atoms of Ga were replaced by Ni to obtain a dopant concentration of 6.25% and 12.5% respectively. Since the substitution of Ni impurity in the GaN lattice was done by replacing the Ga atom, the effect of the structural relaxation has been neglected [18]. When the transition Ni defect is introduced in the GaN, the five fold degenerate d-states split into two degenerate d-states by the crystal field splitting [3]. One of the degenerate d-state involves in the bonding and antibonding with N-p state, while the other act as a non-bonding states (e_g and t_{2g}) as shown in the Fig. 2. Since the t_{2g} band lies above e_g band, the tetrahedral bonding of Ni atom in the GaN structure is confirmed [19]. Thus the spin of the defect state may give rise to the magnetic moment.

Fig. 3 shows the total DOS of 6.25% and 12.5% Ni doped GaN. The half metallic nature is clearly seen in 6.25% when compared to 12.5%. The partial density of states for Ni-3d and N-2p which are given in Fig. 4 shows the p–d hybridization of Ni–N in the bonding state which is responsible for the exchange interaction. The magnetic moment per Ni atom in 6.25% and 12.5% are 1.13 and 1.32 μ_B respectively. But the total magnetic moment in each case are different because Ni atom polarizes the four nitrogen atoms bonding with it. In 6.25% concentration, the three equidistant Ni which bonds with N atoms have a magnetic moment of 0.1808 μ_B and the other N atom has 0.2151 μ_B magnetic moment. Here the magnetic moment depends on distance, if the distance between the Ni-3d and N-2p wave function is small, then strong overlapping of orbital's take place and as a result the spin contribution for magnetization is small. This governs that direct exchange interaction mechanism is responsible for the obtained ferromagnetism in the system. For 12.5% concentration, that is, when two Ga atoms are replaced by Ni calculations are optimized by substituting the Ni atoms at two different sites. Fig. 1a shows the formation of the two Ni atoms which forms a dimer with N atom and the Ni–Ni distance is 3.253 Å [20]. The magnetic moment per Ni atom is found to be 1.13 μ_B and the total moment was also found to decrease when compared to 6.25% concentration. This is due to the interaction of Ni spins via N atom bonded to them. When Ni is substituted as shown in Fig. 1b, the magnetic moment is found to increase per Ni atom (1.32 μ_B) and the system is not energetically favorable when compared to the configuration shown in Fig. 1a. From this we conclude that when Ni–Ni distance is 3.253 Å, the magnetic moment per Ni
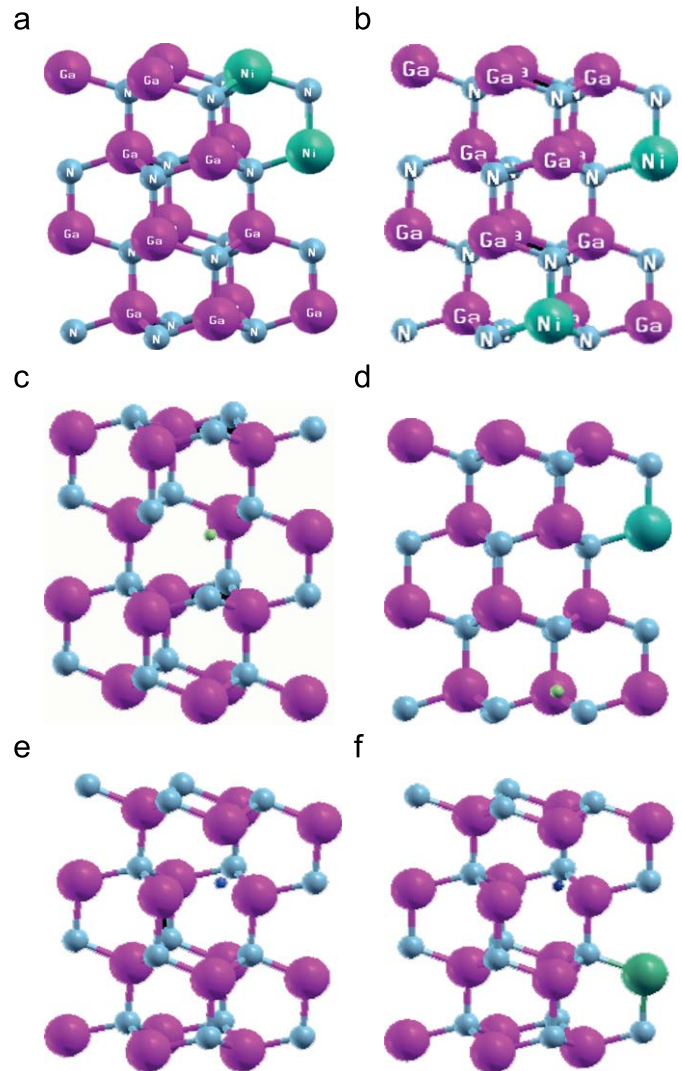

Fig. 1. (a) GaN supercell with two Ni doped to form dimer. (b) GaN supercell with two Ni at different site. (c) GaN supercell with Ga vacancy. (d) Ni doped at Ga site with a Ga vacancy. (e) GaN supercell with N vacancy (f) Ni doped at Ga site with a N vacancy.

atom is 1.13 μ_B and the magnetic moment was less when compared to the 6.25% concentration. For the other position the magnetic moment is found to increase at Ni site. For 12.5% concentration the half metallic nature disappears and it became a ferromagnetic alloy. It is to be noted that increase of Ni–Ni separation in the supercell leads to drastic change in the magnetic coupling. Interestingly it is found that Ni–N distance play an important role in getting maximum magnetization. Similar result is also shown by Wang et al. [21,22] where the author reported the same trend in $Ga_{1-x}Mn_xN$ supercell. So we conclude that only for a small addition of Ni in GaN one can achieve spintronic in these systems.

In order to look for the stability of the nickel dopant in GaN, the formation energy is calculated using the expression [23]

$$E_{for} = E_{sup} + n(E_{Ga} - E_{Ni}) - E_{bulk}$$

where E_{sup} is the total energy of the supercell with n Ga atoms replaced by nickel atoms. E_{bulk} is energy corresponding to bulk. E_{Ga} and E_{Ni} are the energies of the isolated gallium and nickel atoms respectively. The formation energy of 6.25% Ni doped GaN is 0.366 eV. For 12.5% dopant concentration the formation energy is 0.606 eV as per the position given in Fig. 1a, whereas for the