Research articles

Electronic and magnetic behavior of transition metal-doped cubic gallium nitride: first-principles calculations

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ABSTRACT

First-principles calculations within the framework of density functional theory were used to investigate the electronic and magnetic properties of the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ compounds in the zincblende structure, employing the pseudopotential method. The calculated band structures and density of states reveal that the three compounds exhibit a half-metallic behavior and suggest a 100% polarization of the conduction carriers. We found a net magnetic moment of 1.0, 2.0, and 3.0 μ_{β} per supercell, respectively. The results suggest that the compounds may be good diluted magnetic semiconductors for potential applications in spintronics.

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1. Introduction

Over the last few decades, the group III nitride semiconductors, such as gallium nitride (GaN), have been the subject of many theoretical and experimental investigations. This interest is motivated by their applications in high-voltage and optical devices [1], high-temperature microwave applications [2,3]. Their wide direct band gap can be used in optical devices (light emitting diodes, solar cells, photo-detectors) [4–6]. The ground state of gallium nitride is the wurtzite structure (w-GaN). However, depending of the growth techniques, the zincblende phase, i.e. cubic gallium nitride (c-GaN), can be obtained [7]. The difference in total energy between the wurtzite and zincblende structures is quite small (~5.6 meV/atom) [8]. For this reason, the two structures can be grown experimentally. Although c-GaN, the zincblende structure, applications are similar to those developed with w-GaN, it is expected that c-GaN devices will have some advantages and exhibit better performance than the wurtzite phase, because c-GaN has greater crystallographic symmetry and therefore an absence of an internal electric field. Several authors have found advantages for c-GaN compared to w-GaN, such as superior electronic properties, higher drift velocities, higher carrier mobility, and better doping efficiencies [9–11]. During the last few years, GaN has received much attention due of its possible application as a diluted magnetic semiconductor (DMS) for use in spintronics devices. For these applications, ferromagnetism at high a Curie temperature is necessary. Recently, several researcher's have found ferromagnetism at room temperature for GaN doped with a transition metal (TM), both experimentally [12–20] and theoretically [21–29]. All of these investigations of TM-doped GaN have focused on the wurtzite structure, in spite of the fact that many advantages of c-GaN with respect to w-GaN have been reported, and also notwithstanding the fact that over the last few years c-GaN has been grown by means of techniques such as molecular bean epitaxy (MBE) [30–33] and metalorganic chemical vapor deposition [34,35]. Studies of TM-doped c-GaN are very scarce; a few examples are: in 2009, Xingtao et al. [36] studied the magnetic properties of Mn-doped c-GaN using density functional theory; in 2012, Fumiyoshi et al. [33] synthesized Mn-doped c-GaN via MBE; and in 2015, Vilchis et al. [34] synthesized and characterized Mg-doped c-GaN. Additionally, in 2013, Doumi et al. [37] investigated the structural, electronic, and half-metallic ferromagnetic properties of (TM = Mn, Fe)-doped c-GaN by means of first-principles calculations. However, investigations of (TM = Ti, V, and Cr)-doped c-GaN in volume are very rare. For this reason, in the present paper we present a theoretical study of the structural, electronic, and magnetic properties of the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}$-N zincblende structures. It is especially interesting to predict the properties of c-GaN doped with Ti, V and Cr, due to its potential uses in dilute magnetic semiconductors for applications in spintronics.

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2. Computational method

We used the pseudopotential method [38,39] within the framework of density functional theory (DFT) [40,41] as implemented in the Quantum ESPRESSO computational code [42]. In order to take into account the correlation and exchange effects of the electrons, we used the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [43]. A kinetic energy cutoff of 40 Ry was used for the expansion of the wave function in the plane wave. Brillouin zone integrations were performed with the special k-point method over a $6 \times 6 \times 12$ Monkhorst-Pack mesh [44] for each unit cell. All calculations were carried out with spin polarization. According to reference [46], GaN in the zincblende structure has a crystal cubic system, with space group $F\bar{4}3m$ and experimental lattice constant $a = b = c = 4.50$ Å. For the doping concentrations of $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$, only one Ga atom was replaced by a Ti, V, or Cr atom, respectively, inside a supercell with 32-atoms, which corresponds to a $2a \times 2b \times 1c$ tetragonal supercell (see Fig. 1) with space group $P\bar{4}2m$, within the supercell. All atomic positions of pure the c-GaN compound and $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ concentrations were relaxed until all forces became smaller than 10^{-4} eV/Å. The convergence threshold for self-consistent field iteration was 10^{-7} eV.

3. Results and discussions

3.1. Structural properties

Before calculating the electronic structure and the magnetic properties, we carried out volume optimization of c-GaN, $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ in the zincblende structure. For this, we executed a relax calculation (in which all atoms in the supercell move in the three directions) for different values of the lattice constant. For each constant, the crystal total energy was calculated. The data was fit to the Murnaghan equation of state. In this way, the equilibrium parameters, such as the lattice constant (a_0), the bulk modulus (B_0), and the total energy (E_0), can be obtained. Table 1 compares our results with the theoretical and experimental data available from the literature. It can be seen that in the ground state the lattice constant (4.556 Å) for pure zincblende GaN is in very good agreement with the reported experimental result (4.50 Å) [47] and is very close to the theoretical result (4.533 Å) [45]

We note that the values of the bulk modulus of the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ concentrations
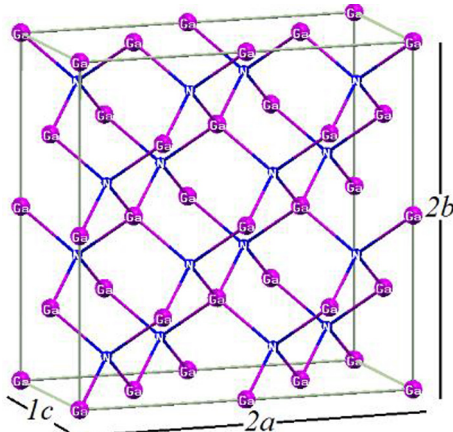
Table 1
Lattice constant, bulk modulus, and total energy of pure GaN, $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ in the zincblende structure.

Compound	a (Å)	B_0 (GPa)	E_0 (eV)
GaN	4.556	201.75	−2693.0518
	4.590[a]	206.90[b]	–
	4.500[c]	190[c]	–
$Ga_{0.9375}Ti_{0.0625}N$	4.522	196.937	−2640.9874
$Ga_{0.9375}V_{0.0625}N$	4.510	199.758	−2663.9599
$Ga_{0.9375}V_{0.0625}N$	4.493	200.516	−2689.6763

[a] Theoretical [45].
[b] Theoretical [46].
[c] Experimental [47].

are very close to the value of the bulk modulus of c-GaN, which confirms that the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ compounds preserve their rigidity. The bulk modulus of pure GaN calculated in the present paper is very close to the theoretical report [46] and in good agreement with experimental results [47].

We observed that in the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ compounds, the equilibrium lattice constant changes slightly with respect to pure GaN. This small change in the parameters may be because the radius of the Ga atom (1.41 Å) is close to the atomic radii of Ti (1.47 Å), V (1.34 Å), and Cr (1.27 Å) atoms. The largest decrease in the lattice constant occurs when a Ga atom is substituted for a Cr atom. This happens due to the fact that of the three transition-metal ions, the Cr atom has the smallest atomic radius, the one farthest from the atomic radius of Ga.

The spin-polarized energy-volume curves of the $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ compounds are shown in the Fig. 2. Energies and volumes are given per unit formula. The results (points on the curves) were fit to the Murnaghan equation of state. It can be seen that in the ground state, the $Ga_{0.9375}Cr_{0.0625}N$ compound is energetically more favorable than $Ga_{0.9375}Ti_{0.0625}N$ and $Ga_{0.9375}V_{0.0625}N$, because it has the lowest energy.
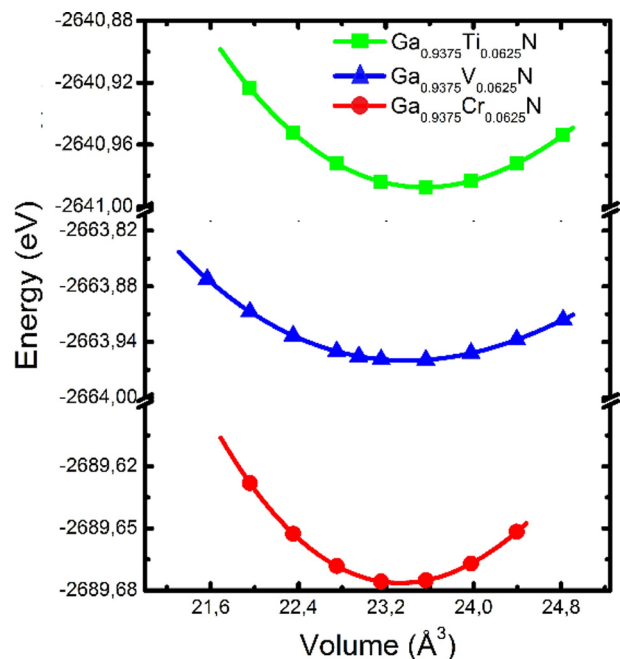
Fig. 2. Total energy versus volume for $Ga_{0.9375}Ti_{0.0625}N$, $Ga_{0.9375}V_{0.0625}N$, and $Ga_{0.9375}Cr_{0.0625}N$ compounds.

Fig. 1. Primitive unit cell of c-GaN compound in the zincblende structure.