Structural and magnetic in c-AlN and c-GaN compound doped with Ti

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Abstract. We report the results of a study with Ti-doped AlN and GaN in the cubic-zincblende phase of the Al0.9375Ti0.0625N and Ga0.9375Ti0.0625N concentrations. All calculations were carried out using the Quantum ESPRESSO code through the pseudopotential method within the framework of density functional theory. The structural results show that the lattice constants of the Al0.9375Ti0.0625N and Ga0.9375Ti0.0625N compounds do not change compared to pure forms of c-AlN and c-GaN, yet the bond length of Ti-N increases compared to the bond length of Ga-N in pure c-AlN and c-GaN. The electronic analyses reveal that both the Al0.9375Ti0.0625N and Ga0.9375Ti0.0625N compounds are ferromagnetic. The Al0.9375Ti0.0625N compound exhibits a metallic behavior with a total magnetic moment of 0.85 µB/cell, whereas Ga0.9375Ti0.0625N exhibits a halfmetallic character with a magnetic moment of 1.0 µB/cell. The magnetic effect in the Al0.9375Ti0.0625N and Ga0.9375Ti0.0625N compounds is the result of a strong hybridization between Ti-3d and N-2p. It is concluded that the Ga0.9375Ti0.0625N compound is a suitable candidate for a diluted magnetic semiconductor with potential use in applications such as spintronics, spin injection or magnetic memories.

1. Introduction

Aluminum and gallium nitride in the cubic zincblende structure (c-AlN and c-GaN) belong to the semiconductor group III. These compounds are characterized by superior physical and chemical properties, such as a high melting point, high thermal stability, high thermal conductivity, large bulk modulus, low compressibility, and large direct band-gap energy [1-2]. In conditions of ambient temperature and pressure, AlN and GaN crystallize in the wurtzite phase, yet experimental researchers have grown AlN and GaN in the zincblende phase. For example, Schupp et al. [3] use molecular beam epitaxy (MBE), and Mohri et al. [4] use reactive pulsed laser deposition to grow c-AlN, while Vilchis et al. [5], via metal organic chemical vapor deposition, and Fumiyoshi et al. [6], through MBE, have grown c-GaN. Since it has been proven that c-AlN and c-GaN can be grown, many investigations have recently studied the c-AlN and c-GaN compounds doped with transition metals [3-6], due to their potential applications in diluted magnetic semiconductors. Studies of Ti-doped c-AlN and c-GaN are scarce, which prompted this theoretical study on the structural, electronic, and magnetic properties of c-AlN and c-GaN doped with Ti, in the Al0.9375Ti0.0625N and Ga0.9375Ti0.0625N concentrations. The results of said study will provide information on the structural and electronic properties of the compounds and lead to the proper understanding of the magnetic behavior of the AlN and GaN semiconductors doped...
with Ti. This research constitutes a starting point for the development of new devices such as ultra-high-density hard disks for computers and other spintronic devices.

2. Computational details

The equilibrium structure parameters such as lattice constant, bulk modulus, bond length, and total energy were calculated using the Quantum ESPRESSO package within the framework of density functional theory \cite{7} by means of the pseudopotential method \cite{8}. In the pseudopotential method, the Kohn-Sham orbital is expanded into plane waves outside the core region and pseudofunctions (pseudopotentials) inside the core. The term of exchange and correlation energy was calculated with the generalized gradient approximation of Perdew, Burke, and Ernzerhof \cite{9}. The kinetic energy cutoff was 40 Ry, with 320 for the charge density. We took a 6×6×12 k-point mesh generated via the Monkhorst-Pack method. Pure AlN and GaN in the zincblende phase were generated in 2x2x1 supercells of 32 atoms. The Al\textsubscript{0.9375}Ti\textsubscript{0.0625}N and Ga\textsubscript{0.9375}Ti\textsubscript{0.0625}N concentrations were reached when one Ti atom occupied the position of one Al (or Ga) atom in the supercell (Figure 1 and Figure 2). Relax-type calculations were performed for pure c-AlN, c-GaN, Al\textsubscript{0.9375}Ti\textsubscript{0.0625}N and Ga\textsubscript{0.9375}Ti\textsubscript{0.0625}N concentrations. The calculations were carried out with spin polarization. The relax calculations ended when the forces became smaller than 10\textsuperscript{-4} eV/Å and the convergence in the energy was 10\textsuperscript{-5} eV.

3. Results and discussions

3.1. Structural properties

The main equilibrium structural parameters such as the lattice constant and bulk modulus of pure c-AlN, c-GaN, Al\textsubscript{0.9375}Ti\textsubscript{0.0625}N and Ga\textsubscript{0.9375}Ti\textsubscript{0.0625}N concentrations in the zincblende phase were calculated. The semi-empirical Murnaghan equation of state was used to minimize the total energy of the supercell versus the volume while the lattice constant was also optimized. Figure 3 shows the energy-volume curve fit to the Murnaghan equation for Al\textsubscript{0.9375}Ti\textsubscript{0.0625}N while Figure 4 shows the same curve for Ga\textsubscript{0.9375}Ti\textsubscript{0.0625}N. Additionally, in order to determine the magnetic behavior, the ferromagnetic (FM) and antiferromagnetic (AFM) phases were also calculated, as shown in Figure 3 and Figure 4.

The equilibrium lattice constants obtained for pure forms of c-AlN and c-GaN were 4.3815 Å and 4.556 Å, respectively. These values are consistent with the theoretical values reported by other authors: 4.38 Å \cite{2}, 4.379 Å \cite{10}, and 4.37 Å \cite{11} for AlN, and 4.59 Å \cite{12} and 4.550 Å \cite{13} for GaN. The values of the lattice constant were are also consistent with the experimental reports, 4.37 Å \cite{14} for c-AlN and 4.50 Å \cite{15} for c-GaN. The bulk moduli calculated for pure binary compounds were 206.52 GPa and 201.75 GPa, respectively. These values are very close to those reported by other authors, 202
GPa [14] for c-AlN and 206.9GPa [13] for c-GaN. The consistent agreement between the calculated values and the theoretical and experimental results guarantees the reliability of the calculations.

The calculated values of the lattice constant and the bulk modulus for Al$_{0.9375}$Ti$_{0.0625}$N were 4.3886 Å and 186.98 GPa, respectively. For Ga$_{0.9375}$Ti$_{0.0625}$N, they were 4.5220 Å and 198.94 GPa. The bond lengths $l_{\text{Al-N}}$ and $l_{\text{Ga-N}}$ (defined as the average of the distances between the Al (or Ga) atom and its first four next neighbors known as the N atoms, see Figures 1 and 2) were computed. For the pure c-AlN and c-GaN compounds, the resulting values were 1.9706 Å and 1.9362 Å, respectively. Similarly, the bond length between Ti-N $l_{\text{Ti-N}}$ for Al$_{0.9375}$Ti$_{0.0625}$N and Ti-N for Ga$_{0.9375}$Ti$_{0.0625}$N were 2.048 Å and 1.9978 Å, respectively. The lattice constant and the bond length $l_{\text{Ti-N}}$ of Al$_{0.9375}$Ti$_{0.0625}$N (a = 4.3886 Å and $l_{\text{Ti-N}}$ = 2.048 Å) are very close to the lattice constant and the bond length $l_{\text{Al-N}}$ of pure c-AlN (a = 4.3815 Å and $l_{\text{Al-N}}$ = 1.9706 Å). Similarly, the lattice constant and the bond length $l_{\text{Ga-N}}$ of Ga$_{0.9375}$Ti$_{0.0625}$N (a = 4.5220 Å and $l_{\text{Ga-N}}$ = 1.9978 Å) are very close to the lattice constant and the bond length $l_{\text{Ga-N}}$ of pure c-GaN (a = 4.556 Å and $l_{\text{Ga-N}}$ = 1.9362 Å). Therefore, the substitution of an Al (or Ga) atom by a Ti atom does not change the zincblende structure of the compound. This occurs because the atomic radii of Al (1.43 Å) and Ga (1.41 Å) are very close of the atomic radius of Ti (1.47 Å).

Finally, as shown in Figure 3 and Figure 4, the FM and AFM phases were calculated for the Al$_{0.9375}$Ti$_{0.0625}$N and Ga$_{0.9375}$Ti$_{0.0625}$N compounds, respectively. For the AFM phase, several spin configurations were calculated until the configuration with the lowest energy was found. Figure 3 and Figure 4 show that both the Al$_{0.9375}$Ti$_{0.0625}$N and Ga$_{0.9375}$Ti$_{0.0625}$N compounds are ferromagnetic, since the FM phase has less energy than the AFM phase. The energy difference $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ was 321 meV for Al$_{0.9375}$Ti$_{0.0625}$N and 665 meV for Ga$_{0.9375}$Ti$_{0.0625}$N.

3.2. Electronic properties
The computed spin-polarized densities of state for the zincblende Al$_{0.9375}$Ti$_{0.0625}$N and Ga$_{0.9375}$Ti$_{0.0625}$N compounds were evaluated with the equilibrium lattices reported in the previous section as well as ultra-soft pseudopotentials and the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof. The density of states (DOS) of the Al$_{0.9375}$Ti$_{0.0625}$N and Ga$_{0.9375}$Ti$_{0.0625}$N compounds are shown in Figure 3. For the DOS, the Fermi level is defined as the zero-point energy.

The DOS of Al$_{0.9375}$Ti$_{0.0625}$N shown in Figure 5 reveals that this compound has a metallic character, because it has spin-up and spin-down states across the Fermi level. In contrast, the DOS of Ga$_{0.9375}$Ti$_{0.0625}$N illustrated in Figure 6 shows that this second compound has a half-metallic behaviour, since the spin-up states are metallic and the spin-down states are semiconductors. Hence, the spin-up states of the Ga$_{0.9375}$Ti$_{0.0625}$N concentrations are partially filled, leading to 100% spin polarization of the conduction carriers. Thus, the Ga$_{0.9375}$Ti$_{0.0625}$N compound fulfills the requirements to be used as a spin injector [16].
Figure 5 and Figure 6 show that the main contribution to the DOS around the Fermi level comes from the Ti atom, with a small contribution from the four nitrogen atoms closest to the Ti atom. Due to the hybridization and polarization that occurs between the d-Ti and p-N states, finite magnetic moments of 0.85 \( \mu_B/\text{cell} \) in Al\(_{0.9375}\)Ti\(_{0.0625}\)N and 1.0 \( \mu_B/\text{cell} \) in Ga\(_{0.9375}\)Ti\(_{0.0625}\)N are created.

4. Conclusions
The structural, electronic, and magnetic properties of the zincblende Al\(_{0.9375}\)Ti\(_{0.0625}\)N and Ga\(_{0.9375}\)Ti\(_{0.0625}\)N compounds were analyzed. It was found that the lattice constant and bond lengths in the Al\(_{0.9375}\)Ti\(_{0.0625}\)N and Ga\(_{0.9375}\)Ti\(_{0.0625}\)N concentrations do not change compared to the binary forms of c-AlN and c-GaN. Therefore, both concentrations preserve their zincblende structure. Regarding the electronic properties, the Al\(_{0.9375}\)Ti\(_{0.0625}\)N and Ga\(_{0.9375}\)Ti\(_{0.0625}\)N compounds exhibited a FM character, with Al\(_{0.9375}\)Ti\(_{0.0625}\)N being metallic and Ga\(_{0.9375}\)Ti\(_{0.0625}\)N half-metallic. The Al\(_{0.9375}\)Ti\(_{0.0625}\)N and Ga\(_{0.9375}\)Ti\(_{0.0625}\)N compounds have magnetic properties, with magnetic moments of 0.85 \( \mu_B/\text{cell} \) and 1.0 \( \mu_B/\text{cell} \), respectively. The half-metallic FM behavior of Ga\(_{0.9375}\)Ti\(_{0.0625}\)N shows that this compound has 100% spin polarization of the charge carriers. This property paves the path for potential applications in diluted magnetic semiconductors, spin injectors, and spintronics.

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