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DFT predictions of ferromagnetism in the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds

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ABSTRACT

We employed density functional theory (DFT) in order to study the structural, electronic, and magnetic properties of pure AlN and C-atom-doped AlN compounds. The calculations were carried out using the method based on pseudopotential, employed exactly as implemented in Quantum ESPRESSO code. For the description of the electron–electron interaction, generalized gradient approximation (GGA) was used. The calculations showed that the substitution of a C atom at the N site introduce a magnetic moment of about 1.0 μ_B, while two C atom substitutions introduce a magnetic moment of about 2.0 μ_B. These magnetic properties become hybridization states C-2p and their first neighboring Al-2p and first neighboring N-2p atoms. Calculated magnetic properties indicate that C-doped AlN compound can potentially be used in diluted magnetic semiconductors.

Introduction

AlN stabilizes in the wurtzite structure in bulk form [1]. AlN, as the largest band-gap semiconductor material, has many superior properties, and thus is the best material for constructing devices in the violet region. It is also used as electronic packaging material and is applied to optical disks as well as lithographic photo masks [2–4]. Aluminum nitride exhibited stability at high temperatures, considerable thermal conductivity, low thermal expansion, and high resistance to gases and chemicals [5]. Recently, AlN has received extensive attention because of its possible use as a diluted magnetic semiconductor (DMS) with potential application in the field of spintronics. For these applications, ferromagnetism at room temperature is a requirement. In recent years, high-temperature ferromagnetism has been reported by many researchers in several types of transition-metal (TM)-doped semiconducting oxides and nitrides [6–8]. However, it was found that the magnetic TM dopants in TM-doped DMS segregate to form ferromagnetic clusters, precipitate, or secondary phases [9–11]. This represents a big obstacle for practical applications of diluted magnetic semiconductors. To avoid this problem, many researchers have focused on investigating the effect of nonmagnetic ion doping in semiconductors in order to obtain high-temperature ferromagnetic semiconductors. Experimental results have proved that it is possible

to obtain high-temperature ferromagnetism in nonmagnetic anion, for example nonmagnetic C- and N-doped ZnO, TiO_2 and C-doped GaN [12–14]. In this paper, we present first-principles total energy calculations of the structural, electronic, and magnetic properties of $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds. First we calculated the structural parameters of pure AlN and the two ternary compounds considered in this study, and then we found the formation energy. Finally, we made a detailed analysis of the band structure and the density of states of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds. We found that the ternary compounds exhibit half-metallic and ferromagnetic behavior, and therefore they can be used in dilute magnetic semiconductors and spintronics.

Computational method

The calculations were performed within the DFT framework using the Quantum ESPRESSO package [15]. The correlation and exchange effects of the electrons were treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [16]. Electron–ion interactions were treated with the pseudopotential method [17,18]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40 Ry. For the charge density, a kinetic energy cutoff of 400 Ry was used. A $6 \times 6 \times 4$ Monkhorst–Pack mesh [19] was used to generate the k-points in the unit cell. The calculations were performed taking into account the spin polarization. To calculate the structural,

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electronic, and magnetic properties of pure AlN, a 32-atom $2a \times 2b \times 2c$ wurtzite supercell was considered. The concentrations $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ were obtained by substituting one and two N-atoms in the supercell in the positions shown in Fig. 1. Pure AlN and the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds were modeled according to the special quasirandom structures approach [20], and the disorder aspects were ignored.

Results and discussions

Structural properties

To determine the structural properties in the ground state, such as the lattice constant (a_0), the bulk modulus (B_0), the c/a ratio, and the total energy (E_0) of pure AlN, $AlC_{0.0625}N_{0.9375}$, and $AlC_{0.125}N_{0.875}$ concentrations in the wurtzite structure, the total energy was calculated as a function of the volume, and the results were fit to the Murnaghan equation of state [21]. Additionally, for the $AlC_{0.0625}N_{0.9375}$ compound, the total energy variation was calculated as a function of the volume for the ferromagnetic (FM) and non-magnetic phases, while for the $AlC_{0.125}N_{0.875}$ compound the ferromagnetic (FM), antiferromagnetic (AFM), and non-magnetic phases were calculated, in order to find the most favorable magnetic phase. Fig. 2 shows the energy–volume curves.

The lattice constant, the c/a value, the bulk modulus (B_0), the total energy (E_0), and the magnetic moment (μ_β) per cell are shown in Table 1.

The lattice constant a and c/a ratio calculated for the pure AlN accords well with values reported experimentally, since it differs by less than one percent. The values of the bulk modules of the pure AlN, $AlC_{0.0625}N_{0.9375}$, and $AlC_{0.125}N_{0.875}$ concentrations are higher, which confirms that they are quite rigid, making them good candidates for possible application in devices operated at high temperatures and high power, as well as in hard coatings.

When one N atom in the $2a \times 2b \times 2c$ supercell is substituted with a C atom, the lattice constant in the $AlC_{0.0625}N_{0.9375}$ compound changes only slightly with respect to pure AlN. We found a similar behavior for the $AlC_{0.125}N_{0.875}$ compound. This small change in the parameters may be because the radius of the C atom (0.914 Å) is very close to the atomic radius of N (0.92 Å).

We can see in Fig. 2(b) that for the $AlC_{0.0625}N_{0.9375}$ compound the calculated total energy of spin polarized state (FM phase) is lower than that of the non-spin polarized state (non-magnetic phase) by about 65.4 meV, while for the $AlC_{0.125}N_{0.875}$ compound,

Fig. 2(c), in the ground state the FM state is lower than the AFM state by about 98.2 meV and the FM state is lower than the non-magnetic state by about 109.6 meV, which indicates that the ground state of C-doped AlN is ferromagnetic.

The spin polarization calculations for the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds result in a magnetic moment of 1.0 and 2.0 per supercell, respectively. A similar magnetic behavior has been found in C-doped GaN [14], ZnO [24], TiO_2 [25], and ZnS [26].

In order to verify the relative stability of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds, we calculated the corresponding formation energy which, is expressed as:

$$E_f = E_{C:AlN} - E_{AlN} - mE_C + mE_N$$

where $E_{C:AlN}$, E_{AlN}, E_C and E_N are the energies of C-doped AlN, pure AlN, an isolated carbon atom, an N atom in the nitrogen molecule, respectively [27]. The integer m is the number of C atoms that substitute for N. We calculated the total energy E_C, E_N, and E_{Al} in their ground states, diamond, molecule, and FFC. The energy values are -11.406 eV, -19.907 eV, and -46.391 eV, respectively. Table 2 shows the calculated values of formation energy E_f.

The value of the formation energy of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds is positive. Therefore, the compounds are metastable, and the moderate formation energy values indicate that the compounds can easily be grown experimentally. Similar results for the formation energy were found by El Amari et al. [28] for the $ZnC_{0.0625}O_{0.9375}$ compound.

These results for the energy of formation are important, because knowing these values, growing conditions can be improved, and therefore $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds of excellent quality can be grown.

Electronic properties

The theoretical lattice constants and c/a ratio of the AlN and the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds, shown in Table 1, were used to calculate the band structure and the spin-polarized density of states (DOS) along the high-symmetry direction in the first Brillouin zone.

The band structure for pure AlN and the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds is shown in Fig. 3. Fig. 3(a) shows the band structure of pure AlN. This confirms the direct semiconductor behavior, with the top of the valence band and the bottom of the conduction band located at the Γ point of the Brillouin zone. We found a direct band gap of about 4.3 eV. The magnitude of this
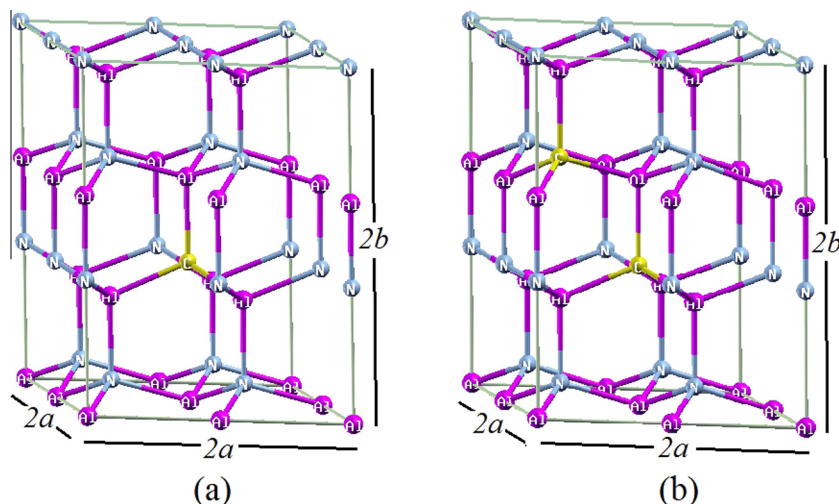

Fig. 1. Unit cell of the ternary compound: (a) $Al_{0.9375}C_{0.0625}N$, (b) $Al_{0.875}C_{0.125}N$ after structural relaxation.
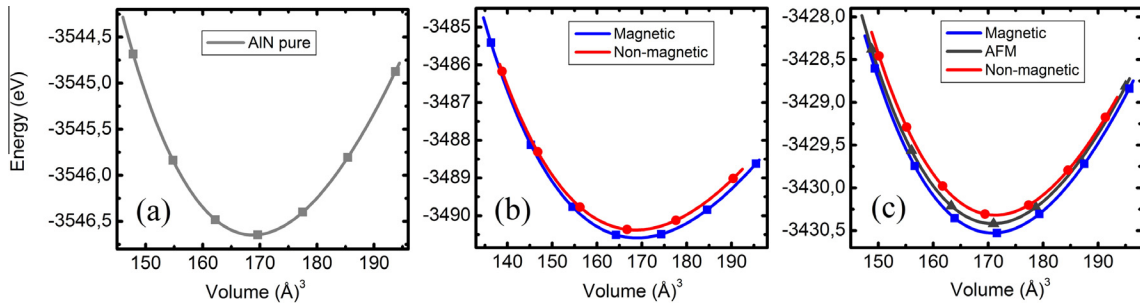
Fig. 2. Total energy as a function of volume for (a) AlN pure, (b) $AlC_{0.0625}N_{0.9375}$, (c) $AlC_{0.125}N_{0.875}$.

Table 1
Lattice constant, c/a ratio, bulk modulus, total energy, and magnetic moment per cell of pure AlN, $AlC_{0.0625}N_{0.9375}$, and $AlC_{0.125}N_{0.875}$.

Compound	a (Å)	c/a	B_0 (GPa)	E_0 (eV)	μ (μ_β/cell)
AlN	3.121	1.603	192.93	−3546.648	0.0
	3.110[a]	1.601[a]	192[b]	–	–
$AlC_{0.0625}N_{0.9375}$	3.127	1.606	182.87	−3490.590	~1.0
$AlC_{0.125}N_{0.875}$	3.129	1.609	184.71	−3434.738	~2.0

[a] Experimental Ref. [22].
[b] Theoretical Ref. [23].

gap is smaller than the value reported experimentally (6.2 eV) for AlN in the wurtzite structure [29]. This occurs because the GGA approximation underestimates the forbidden energy gap in semiconductors. The valence band is mainly determined by Al-2p states, and N-2p makes a minor contribution.

Fig. 3(b and c) shows the band structure of the ternary $AlC_{0.0625}$ $N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds, respectively. We can observe that the majority spin (up) states preserve a band gap, but in the minority spin (down) states there is a penetration toward the prohibited energy zone of the states C-p in a greater proportion and states 2p-N and 2p-Al in a lesser proportion. Therefore, due to the introduction of a C atom into the structure of AlN, it loses its semiconductor nature. The allowed ternary compounds exhibit half-metallic behavior, determined by such states. We can see that the spin down orientation of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$

Table 2
Formation energy.

Compound	E_f (eV)
$AlC_{0.0625}N_{0.9375}$	1.165
$AlC_{0.125}N_{0.875}$	2.125

compounds is partially filled and exhibits dispersed bands above the Fermi level. High polarization of the conduction carriers is confirmed by the fact that the C atom dopants couple ferromagnetically and that there is a high presence of conduction carriers in the minority spin channel. These compounds exhibit a spin polarization of 100% of the conduction carriers, and they are responsible for the conduction in C-doped AlN. This is a requirement for spin injectors [30]. This finding suggests that these ternary compounds can be efficiently used in spintronics.

In order to study the atomic contribution to the ferromagnetism, we calculated the total density of states (TDOS) and local density of states (LDOS) for the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds. Fig. 4(a and b) shows the TDOS and LDOS 2p states of: C atom, the first neighboring Al atom, and the first neighboring N atom. The total density of states confirms that due to the C substitution at the N site, the compound has a half-metallic character. This behavior occurs because in the valence band near the Fermi level, the majority spins are semiconductors, and the minority spins are metallic. Fig. 4(a and b) shows that in the valence band near the Fermi level, the spin-down density is mainly dominated by the C-2p states and to a lesser extent by the Al-2p and N-2p states, which cross the Fermi level. This indicates that all of the magnetic moment comes from 2p orbitals, in which a majority of the magnetic moment comes from partially filled 2p orbitals of the C atom. Fig. 4(b) shows that in the $AlC_{0.125}N_{0.875}$ compound the magnetic moment induced by two C dopant and the corresponding moment distribution are nearly consistent with those in the cases of a single C atom substitution in the supercell.

We can see in Fig. 4 that in the majority spin, the partial density of states belonging to the C-2p orbital exhibits a high peak near the Fermi level, about −0.5 eV for $AlC_{0.0625}N_{0.9375}$ and 0.85 eV for $AlC_{0.125}N_{0.875}$, thus indicating localized states in that region. In the valence band around the Fermi level, the C-2p states overlap with another two peaks of smaller amplitude belonging to N-2p
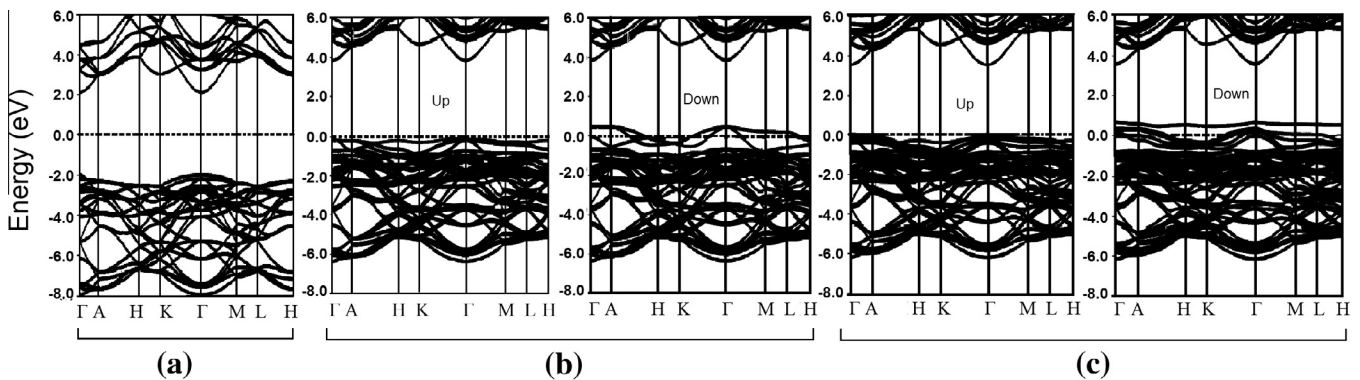

Fig. 3. Electronic energy bands for: (a) pure AlN, (b) $AlC_{0.0625}N_{0.9375}$, and (c) $AlC_{0.125}N_{0.875}$ compounds.
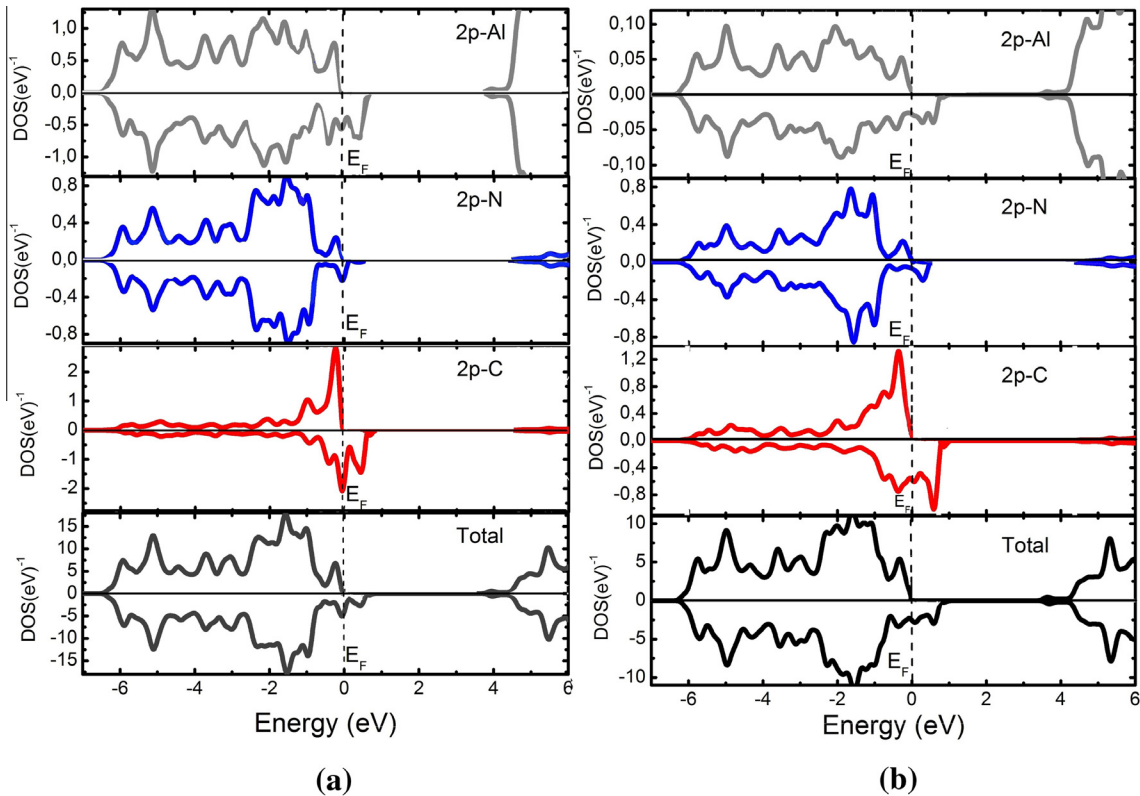
Fig. 4. Partial and total density of states for the allowed ternary compounds (a) $AlC_{0.0625}N_{0.9375}$ and (b) $AlC_{0.125}N_{0.875}$.

and Al-2p. Therefore, there is strong hybridization between the C-2p, N-2p, and Al-2p orbitals. Additionally, the TDOS confirms the presence of some unoccupied bands above the Fermi level, because there is no contribution of spin up and the minority spin exhibits a strong hybridization between the C-2p, N-2p, and Al-2p states, resulting in a magnetic moment of 1.0 μ_B/Cell for $AlC_{0.0625}N_{0.9375}$ and 2.0 μ_B/Cell for $AlC_{0.125}N_{0.875}$. The magnetic moment of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds is an integer. Therefore, this confirms that each compound is magnetic and half-metallic. When we calculated the contribution of each atom to the total magnetic moment, we found that the main contribution to the magnetic moment is by the carbon 2p orbitals (0.77 μ_B), while each of the neighboring N atoms and Al atoms also contribute a small part (0.02 μ_B and 0.20 μ_B, respectively) for $AlC_{0.0625}N_{0.9375}$, whereas for the $AlC_{0.125}N_{0.875}$ compound the local contribution is 0.74 μ_B for the C atom and 0.025 μ_B and 0.063 μ_B for the N and Al atoms, respectively. In both compounds, the main contribution to the magnetic moment comes from the carbon atom. A similar result was obtained by Lin Yu et al. [14] in their first-principles study of the effects of carbon on the ferromagnetism in doped GaN, where the main contribution to the total magnetic moment comes from C.

Conclusions

First-principles total energy calculations to determine the structural, electronic, and magnetic properties of the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}N_{0.875}$ compounds were carried out. The calculated values of the bulk modules were quite high; therefore, the ternary compounds are quite rigid, which makes them attractive for potential applications at high temperatures and for hard coatings. Also, we found that the compounds exhibit magnetic and half-metallic behavior, due to the orbitals 2p-C, 2p-N, and 2p-Al that

cross the Fermi level. Finally, we found that the $AlC_{0.0625}N_{0.9375}$ and $AlC_{0.125}$
$N_{0.875}$ compounds exhibit magnetic properties with magnetic moments 1 μ_B and 2 μ_B per supercell, respectively. These properties show that these compounds are good candidates for possible application in diluted magnetic semiconductors, spin injectors, and other spintronics applications.

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