Effects of substitutions of C atoms by Al and N in the w-AlN compound

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Abstract. We present ab-initio calculations in the pseudopotential approximation for the carbon atoms substitutions by aluminium and nitrogen sites at the AlN compound in wurtzite phase. Structural parameters for the AlN with and without carbon were optimized. Subsequently, the electronic and magnetic properties are determined by the density of states (DOS). Also it was determined that Carbon substitutions (AlN:C) are quite stable. This substitution exhibits magnetic properties, indicating that these compounds are good candidates for possible application in diluted magnetic semiconductors, spin injectors, and other spintronics applications.

1. Introduction

The aluminium nitride (AlN), which crystallizes in the wurtzite structure, is a semiconductor material with a wide band gap of approximately 6.2eV, not only is a suitable material for the design Light-Emitting Diodes (LEDs) and Laser Diodes (LDs) [1], also has been used in electronics and optoelectronics [2]. The AlN present stability to high temperature, a considerable thermal conductivity, low thermal expansion and high resistance to gases and chemicals [3]. 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 [4-6]. However, it was found that the magnetic TM dopants in TM-doped DMS segregate to form ferromagnetic clusters, precipitate, or secondary phases [7-9]. 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 is possible to obtain high-temperature ferromagnetism in nonmagnetic anion, for example nonmagnetic C- and N-doped ZnO, TiO_2 and C-doped GaN [10-12]. 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 $Al_{0.9375}C_{0.0625}N$ compounds. First, we calculated the structural parameters of pure AlN and the two ternary compounds considered in this study. Finally, we made a detailed of the density of states. We found that the ternary compounds exhibit magnetic properties, and therefore they can be used in dilute magnetic semiconductors and spintronics.

2. Computational method

The calculations were performed within the DFT framework using the Quantum ESPRESSO package [13]. The correlation and exchange effects of the electrons were treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [14]. Electron–ion interactions were treated with the pseudopotential method [15,16]. 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 400Ry was used. A 6×6×4 Monkhorst-Pack mesh [17] 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, electronic, and magnetic properties of pure AlN, a 32-atom 2a×2b×2c wurtzite supercell was considered. The concentrations $AlC_{0.0625}N_{0.9375}$ (C by N) and $Al_{0.9375}C_{0.0625}N$ (C by Al) were obtained by substituting one N-atom and one Al-atom, respectively.

3. Results and discussion

3.1. Structural parameters

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 $AlC_{0.0625}N_{0.9375}$ and $Al_{0.9375}C_{0.0625}N$ concentrations in the wurtzite structure, the total energy was calculated as a function of the volume, and the results were fitted to the Murnaghan equation of state [18]. Figure 1 shows the energy-volume curves for $AlC_{0.0625}N_{0.9375}$ (C by N) and $Al_{0.9375}C_{0.0625}N$ (C by Al).
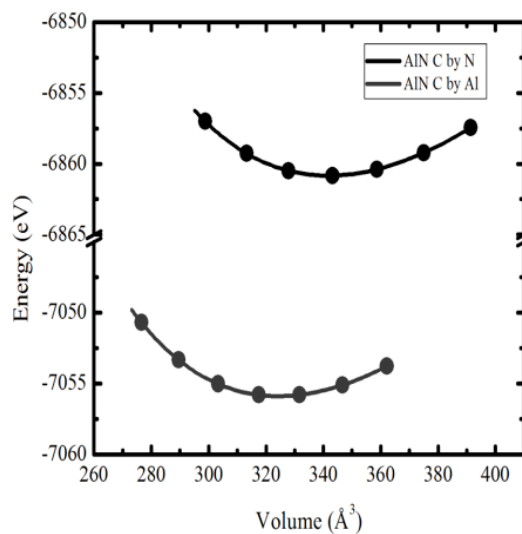

Figure 1. Total energy as a function of volume for AlN:C. Up C by N and bottom C by Al.

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.

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 $_{Al0.9375}C_{0.0625}N$.

Structure	a_0 (Å)	c/a	V_0 (Å^3/atom)	B_0 (GPa)	E_0 (eV/atom)	$\mu(\mu_\beta$/cell)
AlN	3.121	1.602	10.551	192.93	-221.66	0.0
	3.110[a]	1.601[a]	10.432[c]	192[b]	-	
$AlC_{0.0625}N_{0.9375}$	3.129	1.609	10.679	184.71	-214.40	~ 2.0
$Al_{0.9375}C_{0.125}N$	3.084	1.594	10.135	182.88	-220.49	~ 0.4

[a] Experimental Reference [19], [b] Theoretical Reference [20], [c] Experimental Reference [21].

Figure 1 show that $Al_{0.9375}C_{0.0625}N$ compound is energetically most favourable than the $AlC_{0.0625}N_{0.9375}$ compound; additionally, the lattice constant a and c/a ratio calculated for the pure AlN accords well with values reported experimentally [19], 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 $Al_{0.9375}C_{0.0625}N$ concentrations are higher, which confirms that they are quite rigid, making them good candidates for possible application in devices operated at high temperature and high power, as well as in hard coatings.

As we can see in the Table 1, when one N atom in the $2a\times2b\times2c$ 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. This small change in the parameters may be because the radius of the C atom (0.914Å) is very close to the atomic radius of N (0.92Å). Moreover, when one Al-atom is substituted by a C atom, the lattice constant in the $Al_{0.9375}C_{0.0625}N$ compound decreases because the radius of the C atom (0.914Å) is most smaller than the atomic radius of Al (1.43Å). The spin polarization calculations for the $AlC_{0.0625}N_{0.9375}$ and $Al_{0.9375}C_{0.0625}N$ compounds result in a magnetic moment of 2.0 and $0.4\mu_\beta$ per supercell, respectively. Similar magnetic behaviour has been found in C-doped GaN [12] and ZnO [22].

3.2. Electronic properties

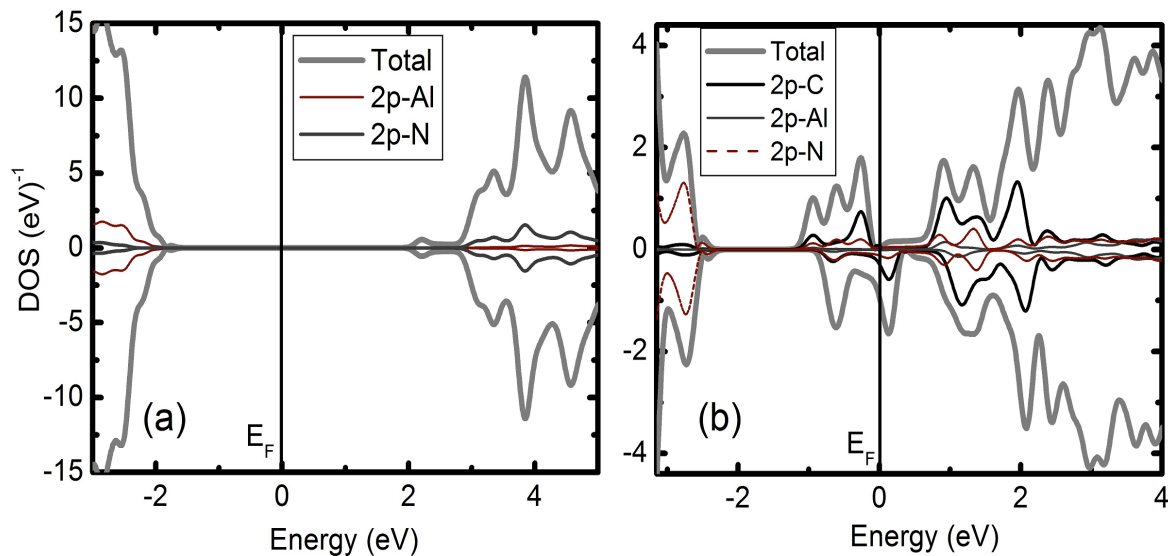Figure 2 shows the total and partial density of states for pure AlN and $AlC_{0.0625}N_{0.9375}$ (C by N) compound.

Figure 2. Total and partial density of states of (a) AlN, (b) $AlC_{0.0625}N_{0.9375}$

Figure 2(a) show the density of state pure AlN. This confirms the semiconductor behaviour. Figure 2(b) show the density state of the ternary $AlC_{0.0625}N_{0.9375}$ compound. We can observe that the majority spin (up) states preserve a band gap, but in the minority spin (down) states there is a penetration towards the prohibited energy zone of the state C-p in greater proportion and states 2p-N and 2p-Al in lesser proportion. Therefore, due to the introduction of a C atom into the structure of AlN, it loses its semiconductor nature. The allowed ternary compound exhibit half-metallic behaviour, determined by such states. We can see in Figure 2(b) 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 -0.4eV for $AlC_{0.0625}N_{0.9375}$ 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 N-2p and Al-2p. Therefore, there is strong hybridization and polarization 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 and polarization between the C-2p, N-2p, and Al-2p states, resulting in a magnetic moment of $2.0\mu_\beta$ the main contribution to the magnetic moment comes from the carbon atom. A similar result was obtained by Lin Yu et al. [12] in their first-principles study of the effects of carbon on the ferromagnetism in doped GaN.

4. Conclusions

First-principles total energy calculations to determine the structural, electronic, and magnetic properties of the $AlC_{0.0625}N_{0.9375}$ and $Al_{0.9375}C_{0.0625}N$ 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 properties with magnetic moments $2\mu_\beta$ and $0.4\mu_\beta$ 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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