DFT applied to the study of carbon-doped zinc-blende (cubic) GaN

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Abstract. Employing first principles within the framework of density functional theory, the structural properties, electronic structure, and magnetism of C-doped zincblende (cubic) GaN were investigated. The calculations were carried out using the pseudopotential method, employed exactly as implemented in Quantum ESPRESSO code. For GaC0.0625N0.9375 concentration, a metallic behavior was found. This metallic property comes from the hybridization and polarization of C-2p states and their neighboring N-2p and G-4p states.

1. Introduction
Gallium nitride (GaN) is one of the III-nitride semiconductors. This material has been the subject of many intense investigations over the last few decades due to potential applications for optical devices [1] and in high-voltage, high-power, and high-temperature microwave applications [2, 3]. They are wide-band-gap semiconductors and are used for short-wavelength electroluminescent devices. Additionally, heterostructures based on the surface growth of oxides on GaN are used in various applications, such as high-efficiency blue and green light-emitting devices, ultraviolet light-emitting diodes, metal-oxide-semiconductor field-effect transistors, and field-effect transistors [4–6]. The ground state of GaN is the wurtzite structure. However, depending on the substrate and the growth conditions, a zinc-blende phase can be formed [7]. The difference in total energy between the zinc-blende and wurtzite structures is very small (~10meV/atom), which explains why the two structures can be obtained experimentally. On the other hand, for a long time, carbon has been considered an atmospheric impurity that could contaminate semiconductor devices based on GaN during the manufacturing process. In particular, carbon contaminant behavior for materials such as GaAs, AlAs, and InAs grown via molecular beam epitaxy has been reported [8, 9]. However, recent theoretical studies show that carbon-doped wurtzite GaN exhibits a metallic behavior [9] and acquires magnetic properties with a magnetic moment of 0.7µμ/atom [10]. Additionally, recently pioneering theoretical research carried out by Espitia et al. [11] has shown that graphene on the GaN(0001) wurtzite surface is stable and the Dirac cones remain intact. However, theoretical or experimental investigations of carbon-doped zinc-blende (cubic) GaN are scarce. For this reason, in this paper we present a systematic theoretical study of the structural, electronic, and magnetic properties of carbon-doped zinc-blende (cubic) GaN.

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2. Computational method

The calculations were carried out within the DFT framework using the Quantum Espresso package [12]. The correlation and exchange effects of the electrons were considered using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [13]. Electron–ion interactions were dealt with via the pseudopotential method [14, 15]. The electron wave functions were expanded into plane waves with a kinetic-energy cutoff of 40Ry. For the charge density, a kinetic energy cutoff of 400Ry was used. The calculations were performed taking into account the spin polarization due to the presence of the Cr atom. To calculate the lattice constant, the bulk modulus, and the total energy of each studied superlattice, the calculated data were fit to the Murnaghan equation of state [16]. To calculate the structural, electronic, and magnetic properties of pure GaN, a 32-atom 2ax2bx1c zincblende supercell was considered. The concentration of GaC_{0.0625}N_{0.9375} was obtained by substituting for one N-atom in the zinc-blende supercell. Pure GaN and the GaC_{0.0625}N_{0.9375} compounds were modeled according to the special quasirandom structures approach [17], and the disorder aspects were ignored.

3. Results and discussions

3.1. Structural properties

![Figure 1. Total energy as a function of the volume for pure GaN (black), GaC_{0.0625}N_{0.9375} (red).]

In order to determine the structural properties in the ground state, such as the lattice constant (\(a_0\)), the bulk modulus (\(B_0\)), the total energy (\(E_0\)), and the magnetic moment (\(\mu\)) per supercell of pure GaN and GaC_{0.0625}N_{0.9375} concentration in the zincblende structure, the total energy was calculated as a function of the volume, and the results were fit to the Murnaghan equation of state [16]. It can be seen that pure GaN and GaC_{0.0625}N_{0.9375} compound are stable or metastable, because in each of the energy-volume curves there is a minimum energy value.

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

| Compound | \(a_0\) (Å) | \(V_0\) (Å³) | \(B_0\) (GPa) | \(E_0\) (eV) | \(\mu\) (\(\mu_\beta\)) |
|----------|--------------|-------------|-------------|-------------|----------------|
| GaN      | 4.533        | 23.258      | 175.75      | -2693.05    | 0              |
|          | 4.552\textsuperscript{a} | 23.58\textsuperscript{a} | 175.32\textsuperscript{a} | -            | -              |
|          | 4.59\textsuperscript{b} | -           | -           | -           | -              |
| GaC_{0.0625}N_{0.9375} | 4.543 | 23.454 | 171.73 | -2685.59 | 0 |

\textsuperscript{a}Theoretical reference [18], \textsuperscript{b}Theoretical reference [19].
We can see in the lattice constant a calculated for the pure GaN agrees well with values reported theoretically, since it differs by less than one percent. The values of the bulk modules of pure GaN and GaC_{0.0625}N_{0.9375} compound 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. When one N atom in the 2ax2bx1c supercell is replaced with a C atom, the lattice constant in GaC_{0.0625}N_{0.9375} compound changes only slightly with respect to pure GaN. This small change in the parameters may be due to the fact that the radius of the C atom (0.914Å) is very close to the atomic radius of N (0.92Å). A similar result has been reported by Espitia et al [9] for GaC_{0.25}N_{0.75}, GaC_{0.50}N_{0.50}, and GaC_{0.75}N_{0.25} compounds in the wurtzite structure.

In order to verify the relative stability of GaC_{0.0625}N_{0.9375} compound, we calculated the corresponding formation energy, which is expressed as:

\[
E_f = E_{C:GaN} - E_{GaN} - nE_C + nE_N
\]

where \(E_{C:GaN}\), \(E_{GaN}\), \(E_C\) and \(E_N\) are the energies of C-doped GaN, pure GaN, an isolated carbon atom, and a N atom in the nitrogen molecule, respectively [20]. The integer \(n\) is the number of C atoms that substitute for N. We calculated the total energy \(E_C\) and \(E_N\) in their ground states, graphite and molecule. The energy values are -11.406eV and -19.90eV, respectively. The calculated value of formation energy \(E_f\) for GaC_{0.0625}N_{0.9375} is -0.751eV. The value of the formation energy of GaC_{0.0625}N_{0.9375} compound is negative. Therefore, the compound is thermodynamically stable, and the moderate formation energy values indicate that the compounds can easily be grown experimentally.

3.2. Electronic properties

The theoretical lattice constants of GaN and GaC_{0.0625}N_{0.9375} compound, 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 GaN and GaC_{0.0625}N_{0.9375} compound are shown in Figure 2. Figure 2(a) shows the band structure of pure GaN. This confirms the direct semiconductor behavior, with the top of the valence band and the bottom of the conduction band located at the \(\Gamma\) point of the Brillouin zone. We found a direct band gap of about 1.78eV. The magnitude of this gap agrees well with values reported theoretically [18].

![Figure 2. Band structure: (a) pure GaN, (b) GaC_{0.0625}N_{0.9375} compound.](image-url)
Figure 2(b) shows the band structure of the ternary GaC$_{0.0625}$N$_{0.9375}$ compound. We can observe that there is a penetration towards the prohibited energy zone. Therefore, due to the introduction of a C atom into the structure of GaN, it loses its semiconductor nature. The allowed ternary GaC$_{0.0625}$N$_{0.9375}$ compounds exhibit metallic behaviour.

Figure 3. Partial and total density of states for the allowed ternary compounds (a) pure GaN and (b) GaC$_{0.0625}$N$_{0.9375}$ compound.

Figure 3(a) shows the total and partial spin-polarized density of states of pure GaN in the zinc-blende structure. The total density of states confirms that pure GaN exhibits semiconductor behavior, determined mainly by the 2p-N and 4p-Ga states. Figure 3(b) shows the total and partial spin-polarized density of states of GaC$_{0.0625}$N$_{0.9375}$ compound zinc-blende structure. The total density of states confirms that due to the C substitution at the N site, the compound has a metallic character. This behavior is mainly dominated by the C-2p states and to a lesser extent by the N-2p and 4p-Ga states. Similar results were reported by Yu et al. [21] in their study of carbon-doped GaN in the wurtzite structure using DFT and by Murillo et al. [22] in their study of the effects of C for N and C for Al in the w-AlN compound.

4. Conclusions

In this work, we carried out first-principles calculations in order to study the structural, electronic, and magnetic properties of pure GaN and GaC$_{0.0625}$N$_{0.9375}$ compound in the zinc-blende structure, within the framework of density functional theory (DFT). The calculated structural parameters agree well with values reported theoretically. The calculated values of the bulk modules of pure GaN and the GaC$_{0.0625}$N$_{0.9375}$ compound are quite high; therefore, these compounds are quite rigid, which makes them attractive for potential applications at high temperatures and for hard coatings. On the basis of the density of states, we found that the GaC$_{0.0625}$N$_{0.9375}$ compound exhibits a metallic behavior determined by the C-2p, N-2p, and Ga-4p states.

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