Theoretical investigation of GaN carbon doped

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Abstract. In this work we used first principles calculations in the frame of density functional theory (DFT) in order to study the structural and electronic properties of GaN doped with carbon. The computational calculations were carried out by a method based on plane waves pseudopotentials, as implemented in the Quantum Espresso code. In the wurtzite type GaN supercell the nitrogen atoms were replaced by carbon atoms (C by N) and then also the gallium atoms by carbon atoms (C by Ga). The carbon concentrations in the GaN volume was set as x=25, 50 y 75%. For each concentration x of carbon the formation energy was calculated for the substitutions C by N and CxGa. We found that it is more energetically favourable that the carbon atoms occupy the positions of the nitrogen atoms (C by N), because in all the x concentrations of carbon the formation energies were lower than that in the substitutions (C by Ga). It was found that the new compounds CxGaN1-x have higher bulk moduli. So they are very rigid. This property makes them good candidates for applications in hard coatings or devices for high power and temperatures. Analysis of the density of states show that the new CxGaN1-x ternary compound have metallic behaviour that comes essentially from the hybridization states N-p and C-p cross the Fermi level.

1. Introduction
Gallium nitride (GaN) is one of the wide direct band gap semiconductors that normally crystallizes in the wurtzite structure [1] it can be used in optoelectronic components, like blue light emitting diodes and lasers [2]. Due to its notable thermal and chemical stability, it is also ideally suitable for the applications in harsh environments, such as high pressure and temperature [2,3]. Large piezoelectric constants of GaN point out to possible applications of GaN-based materials in sensors. Due to wide band gap, these sensors are expected to operate in a broad temperature range and/or in a harsh environment. On the other hand, the carbon in the GaN had not been sufficiently studied. For many years carbon was considered an atmospheric impurities that could contaminate the semiconductor devices based on GaN during the manufacturing process [4,5]. In particular, the carbon polluting behaviour was reported for GaAs, AlAs and InAs grown by Molecular Beam Epitaxy [5]. However, in recent years some theoretical and experimental studies have concluded that the introduction of carbon in the GaN volume strongly alters their electronic and magnetic properties. H. Tang et al [6] at 2001 and R. P. Vaudo et al [7] at 2003 found that the incorporation of carbon in the GaN films generate in an insulating material with higher resistance >10⁸Ω [8,9], for this reason GaN films are becoming increasingly popular in their highly resistive form to be used as insulating buffer layers or substrates in GaN-based device technology.
In this work we execute first principles calculations to investigate the effects of the incorporation of C in the GaN volume on structural and electronic properties of C:GaN system. First, in the GaN structure wurtzite we replaced gallium atoms by carbon atoms (C by Ga) and then nitrogen atoms by carbon atoms (C by N), with carbon concentration of 25, 50 and 75%. We calculate the formation energy of each substitution to find the energetically most favorable configurations.

2. Computational method
To determine the equilibrium geometry of the CₓGa₁₋ₓN y CₓGaN₁₋ₓ (x=0.25, 0.50, 0.75), compounds, in the wurtzite structure the volume and the c/a ratio was optimized. We used the pseudopotential plane-wave method, as implemented in the Quantum espresso code [10]. The correlations and exchange effects are treated using the generalized gradient approximation (GGA). The formation energy of the ternary phase is defined as [11].

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\Delta E = E_{C:GaN} - N_C E_C - N_{Ga} E_{Ga} - N_N E_N
\]  

(1)

Where \(E_{C:GaN}\) is the total energy of the ground state for the corresponding concentration of C by Ga or C by N in the ternary compound. \(E_C\) is the total energy of carbon in the ground state (graphite), \(N_C\) is the number of carbon atoms in the compound. \(E_{Ga}\) is the total energy of ground state of Ga, \(N_{Ga}\) is the number of carbon atoms, \(E_N\) is the total energy of ground state of N and \(N_N\) is the number of nitrogen atoms in the ternary compound.

3. Results and discussions

3.1. Structural properties
The Table 1 show the formation energy calculated with the Equation (1) for ternary CₓGa₁₋ₓN and CₓGaN₁₋ₓ (x=0.25, 0.50, 0.75) compounds.

| %     | Formation energy (eV) |
|-------|-----------------------|
| C by N 0.25 | -3.714                |
| C by N 0.50 | -0.286                |
| C by N 0.75 | 2.345                 |
| C by Ga 0.25 | -0.612                |
| C by Ga 0.50 | 2.586                 |
| C by Ga 0.75 | 10.612                |

For all concentrations, the formation energy is lower when a carbon atom occupies the position of a nitrogen atom, therefore, it is energetically more favourable that the carbon atoms occupy the positions of the carbon atoms in the GaN wurtzite type. Additionally, the ternary C₀.₂₅Ga₀.₇₅N y C₀.₀₅GaN₀.₉₀ has negative formation energy, therefore this compound are thermodynamically stable, whereas that formation energy of C₀.₇₅Ga₀.₂₅ compound is positive, which implies that this compound is thermodynamically unstable, this means that this compound cannot grow under equilibrium conditions, so in order to grow them, it is necessary to supply power to the system, in agreement with the result obtained by Zhang y S. Veprek [12] in their first principles study of metastable phases and thermodynamic modelling of Ti₀.₅Al₀.₅N compound.

The Table 2 shows the main structural parameters of GaN and the allowed ternary compounds. The structural parameters of the binary GaN compound calculated in this work accords well with values reported theoretically [1] and experimentally [13], since it differs by less than one percent. The Table
I show that by increasing the concentration of carbon atoms, the lattice constants of ternary compounds only change slightly with respect to GaN, this may be because the radius of the C atom (0.914Å) is very close to the atomic radius of N (0.92Å). The Figure 1(a) show the variation of the bulk modulus as a function of concentrations of C, whereas the Figure 1(b) show the variation of total energy as a function concentrations of C. The bulk modulus decreases with the increasing amount (x) of the concentration of C atoms with respect to bulk modulus of GaN, whereas that energy total increases linearly (is less negative) with an increasing of the concentration of C atoms in the GaN compound.

Table 2. Structural parameters lattice constant ($a_0$), ratio c/a, bulk modulus ($B_0$) and total energy ($E_0$) of the compounds.

| Compound                  | $a_0$ (Å) | c/a   | $V_0$ (Å$^3$) | $B_0$ (GPa) | $E_0$ (eV) |
|---------------------------|-----------|-------|---------------|-------------|------------|
| GaN                       | 3.2048    | 1.633 | 23.286        | 175.33      | -2693.128  |
| C$_{0.25}$GaN$_{0.75}$    | 3.1986$^a$| 1.6339$^a$ | 23.153$^a$        | 176.54$^a$  | -2693.128  |
| C$_{0.50}$GaN$_{0.50}$    | 3.2120    | 1.6311| 47.41         | 153.35      | -2633.743  |
| C$_{0.75}$GaN$_{0.25}$    | 3.2141    | 1.6360| 56.10         | 146.04      | -2604.074  |

$^a$Theoretical reference [1], $^b$Experimental reference [13].

Figure 1. (a) Bulk module GPa) as a function of concentration of carbon atoms. (b) Total energy as a function of concentration of carbon atoms for C$_x$GaN$_{1-x}$ (x=0.25, 0.50 y 0.75) compounds. In the figures the lines are only a guide to the eye.

3.2. Electronic properties

The Figure 2(a) show the total and partial density of states of the of GaN clean, this compound has a semiconductor behaviour with a forbidden energy gap of 2.0eV. The magnitude of this gap is smaller than the experimentally reported for GaN in wurtzite structure, this occurs because the GGA approximation underestimates the forbidden energy gap in semiconductors. The Figures 2(b), 2(c) and 2(d) shows the total and partial spin-polarized density of states of the ternary C$_{0.25}$GaN$_{0.75}$, C$_{0.50}$GaN$_{0.50}$ y C$_{0.75}$GaN$_{0.25}$ compounds. Due to the introduction of the C atoms in the structure of GaN, it loses its semiconductor nature, there are a penetration towards prohibited energy zone of the states C-p in greater proportion and the states N-p in lesser proportion, therefore, the allowed ternary compounds has metallic behaviour determined by such states.
4. Conclusions

In this work we executed a study of GaN carbon doped, with concentrations of carbon atoms of x = 25%, 50% y 75%, using the Density Functional Theory DFT in the frame pseudopotential plane wave. The formation energy calculations reveal that is more favourable that the carbon atoms occupy the positions of the nitrogen atoms in the GaN wurtzite type. We found that the allowed ternary \( \text{C}_{0.25}\text{GaN}_{0.75} \), \( \text{C}_{0.5}\text{GaN}_{0.5} \) y \( \text{C}_{0.75}\text{GaN}_{0.25} \) have higher bulk moduli, so they are very rigid. This property makes them good candidates for applications in hard coatings or devices for high power and temperatures. The density states studies reveal that there are a penetration towards prohibited energy zone of the states C-p in greater proportion and the states N-p in lesser proportion, therefore, the allowed ternary compounds has metallic behaviour.

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