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Structural, electronic and magnetic properties of Ti-doped polar and nonpolar GaN surfaces

Victor Mendoza-Estrada [a,b,*], Alvaro González-García [a], William López-Pérez [a], Carlos Pinilla [a], Rafael González-Hernández [a]

[a] Grupo de Investigación en Física Aplicada, Departamento de Física, Universidad del Norte, Barranquilla, Colombia
[b] Departamento De Ciencias Naturales y Exactas, Universidad De La Costa, Calle 58 No. 55-66, Barranquilla, Colombia

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ABSTRACT

Based on density functional theory, first-principles calculations were performed in order to study the titanium incorporation on polar and nonpolar GaN surfaces. The formation energy calculations indicate that Ti impurity atoms prefer to incorporate in surface layers (first and second) of GaN. It is also concluded that the incorporation of Ti atoms in Ga-substitutional sites are more energetically favorable compared with N-substitutional or interstitial sites on the polar and nonpolar GaN surfaces. For Ti-rich growth conditions, formation energy calculations show the formation of Ti_xN layers on the *a* and *c* GaN surfaces, which corroborates recent experimental observations. Results also display that the 3*d*-Ti states are the responsible for the metallization of the surface on the *c* and *m* planes, forming an intermetallic alloy (Ti_xN), which could be used as low-resistance ohmic contacts for GaN. In addition, the magnetic properties with Ti doping show magnetization of about 1.0 μ_B/Ti atom for the nonpolar GaN surfaces.

1. Introduction

Gallium nitride (GaN) is one of the wide direct band gap semiconductors, which has a broad range of potential applications for optoelectronic and high power electronic devices. Intensive research over the recent years have made the manufacturing of light emitting diodes (LEDs) in the short wave lengths range, i.e. blue and violet, a commercial reality [1,2]. Its high thermal conductivity also opens new directions for high-temperature/high-power electronic devices [3], as metal-semiconductor field effect transistors (MESFETs), high electron mobility transistors (HEMTs) and heterojunction bipolar transistors (HBTs) [4]. Therefore, a great deal of effort has been directed not only to the growth of high-quality GaN films but also to the achieving of high-quality metal contacts. However, a lot of aspects of GaN and related properties remain to be identified and developed. As it is known, there are two main issues in the GaN-based heterostructures grown along the [0001] direction: the large spontaneous polarization and dense dislocation. In order to reduce the effects of polarization-induced electric field, growing nonpolar or semipolar films, in which the growth direction that is not (0001), is required [5–8].

On the other hand, the formation of low resistance ohmic contacts on the GaN surfaces is also one of the ways of maximizing the quantum efficiency of the GaN-based high electron mobility transistors. For the *c*-GaN plane, Ti/Al-based metal contacts have been widely investigated because Ti/Al-based schemes easily formed low-resistance ohmic contact when annealed above 600 °C [9–12]. Recently, Ti/Al-based contacts on nonpolar [13,14] and semipolar [15,16] n-GaN planes revealed different electrical properties from that on polar n-GaN. Therefore, it is important to carry out a study of the structural stability and electronic properties of the Ti atomic interaction on the polar and nonpolar GaN surfaces. This article investigates the structural, electronic and magnetic properties of Ti-doped polar and nonpolar GaN surfaces using first-principle calculations.

2. Computational methods

The calculations were performed using the first principles pseudo-potential method within the density functional theory (DFT) framework. Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Perdew-Burke-Ernzerhof functional (PBE) [17]. The core electrons were described by the projector augmented wave (PAW) method [18,19], wherein the 3*d* states for Ga were included as valence electrons. The calculations were performed using the

* Corresponding author at: Grupo de Investigación en Física Aplicada, Departamento de Física, Universidad del Norte, Barranquilla, Colombia.
E-mail addresses: evictor@uninorte.edu.co, vmendoza@cuc.edu.co (V. Mendoza-Estrada).

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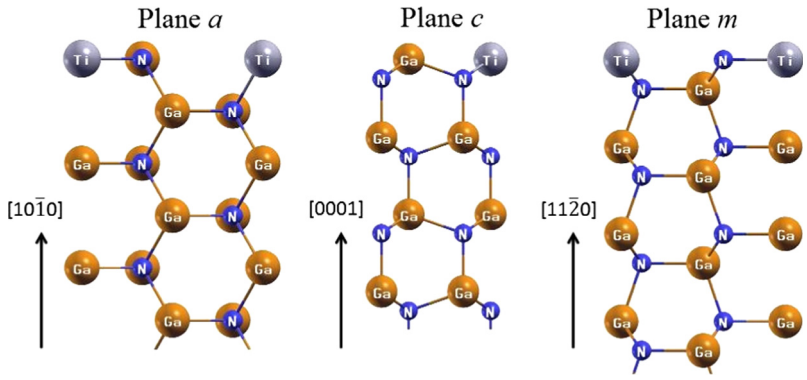

Fig. 1. Structures of the a, c, and m planes of GaN doped with Ti_{Ga}. The structures with Ti_{Ga} in the first layer are shown: (1/0/0) configuration.

vienna ab initio simulation package (VASP) [20,21]. The electron wave function was expanded in plane waves up to a cutoff energy of 500 eV. A gamma-centered grid of $4 \times 4 \times 1$ and $6 \times 6 \times 1$ k-point has been used to sample the irreducible Brillouin zone of the polar and nonpolar systems respectively, in the Monkhorst-Pack special scheme [22]. Methfessel-Paxton smearing technique with a smearing width of 0.10 eV was adopted [23]. These parameters ensure a convergence better than 1 meV for the total energy. We employed a 1×1 surface supercell consisting of a symmetric slab of eleven and sixteen GaN layers for the a and m planes, respectively. The polar c plane calculations were performed using a 2×2 surface supercell with an asymmetric slab geometry consisting of eight c plane layers (see Fig. 1). Undesirable charge transfer was prevented by the passivating of the bottom layers by pseudo-hydrogen atoms. For the Ga-terminated c plane, the 1.25 e fractional charges associated with the dangling bonds in the N bottom layer were saturated with pseudo-hydrogen atoms, each with a fractional charge of 0.75 e. A vacuum thickness of ~12.0 Å has been used throughout the calculations. The surface stoichiometry is not the same for all the studied configurations, the formation energies depend upon the chemical potential of the atomic species in excess. The relative stability among various Ti-doped a, m and c planes, are assessed using the relative formation energy (E_f) given by:

$$E_f = E_{total} - E_{ref} - \Delta\eta_{Ti}\mu_{Ti} - \Delta\eta_{Ga}\mu_{Ga} - \Delta\eta_N\mu_N \quad (1)$$

where E_{total} is the total energy of the configuration under consideration, E_{ref} is the total energy of the reference configuration, in this case the clean polar and nonpolar GaN surfaces, μ_{Ti} is the chemical potential of the Ti atoms and $\Delta\eta_{Ti}$ is the excess or deficit of Ti atoms with respect to the reference; similar definitions hold for $\Delta\eta_{Ga}$ and $\Delta\eta_N$. For Ti incorporation processes, a large number of configurations with different amounts of Ti atoms in substitutional Ga sites were studied. These configurations are labeled as ($l_1/l_2/l_3$), where l_1, l_2 and l_3 are the numbers of Ti atoms in the first, second and third layer, respectively, beginning from the top surface layer.

3. Results and discussion

Before starting the surface calculations, we first optimized the structural parameters for GaN in the wurtzite structure, which is the most stable phase of GaN at low temperatures and pressures. The following lattice parameters were obtained: $a = 3.218$ Å, $c = 5.242$ Å, and the internal parameter $u = 0.377$. These lattice parameters are in good agreement with the experimental (theoretical) data reported by other authors $a = 3.189$ Å, $c = 5.189$ Å and $u = 0.375$ ($a = 3.245$ Å, $c = 5.296$ Å and $u = 0.376$) [24,25]. The optimized parameters for GaN were used to build the slab for the polar and nonpolar GaN supercells (see Fig. 1). On the other hand, the formation enthalpy per atom pair of GaN (ΔH_f^{GaN}) is calculated as:

$$\Delta H_f^{GaN} = \mu_{GaN} - \mu_{Ga} - \mu_N \quad (2)$$

where μ_{GaN} is the total energy per atom pair of the compound GaN, μ_{Ga} the energy per atom of bulk Ga and μ_N is the energy per N atom in the N_2 dimer or the condensed N_2 phase; a positive (negative) value of ΔH_f^{GaN} represents an endothermic (exothermic) reaction. Our result for ΔH_f^{GaN} (−0.99 eV) is in good agreement with the experimental (−1.08 eV) finding [26].

In order to study the effect of the titanium incorporation on the polar and nonpolar GaN surfaces, we have carried out surface formation energy calculations for the titanium atoms at different incorporated configurations on the a, c, and m planes. We found that a titanium atom located in the N-substitutional sites and interstitial positions is energetically unstable with respect to Ga-substitutional sites (Ti_{Ga}). We conclude that in the region close to the polar and nonpolar GaN surfaces, Ti impurity is mainly found in the Ga-substitutional site. Similar results were proposed by Ortega-Lopez et al. [12] and Xiong et al. [27] for Ti doped on the GaN(0001)-2×2 surface and bulk GaN respectively.

In Fig. 1, the supercell structures of the non-polar, a and m planes, and the polar, c plane, are shown, with the substitution of a Ga atom by Ti (Ti_{Ga}) in the first layer, (1/0/0) configuration. The nonpolar a and m planes as well as the polar c plane were constructed by means of the stacking of the GaN primitive cell with the hexagonal wurzite structure, with empty regions along the z axis.

It can be seen in Table 1 that the average distance between the bonds of the impurity of Ti and the N atoms ($d_{Ti\text{-}N}$) of the three layers of the a, c, and m planes decreases after the atomic relaxation. Therefore, a distorted environment around the Ti_xN layers is produced due to Ti_{Ga}. This could be attributed to the difference in the ionic radius of Ti (0.68 Å) and Ga (0.62 Å) atoms.

In order to study the stability of Ti_{Ga} in the nonpolar, a and m planes and the polar, c plane, the formation energy when a Ga atom is replaced by a Ti atom in the first three layers of GaN was calculated. The results are shown in Table 1, where it can be seen that for the a plane, the formation energy is lower when Ti_{Ga} is substituted in the first layer, while for the c (m) plane the formation energy is lower when the Ti_{Ga} impurity is incorporated into the second layer. These results imply that for the a plane the Ti atoms are incorporated into the structure with difficulty. Therefore, the Ti atoms prefer to form bonds with the N atoms on the surface. Nevertheless, the Ti_{Ga} is more likely for the c and m planes in the structure.

On the other hand, in the (1/0/0) and (0/1/0) configurations of the a plane and the (1/0/0) and (0/0/1) of the m plane, the total