

Charged vacancy defects in an AlN nanosheet: A first-principles DFT study

William López-Pérez^{a,*}, Luz Ramírez-Montes^a, Alvaro González-García^a, Carlos Pinilla^a,
Jagger Rivera-Julio^b, Rafael González-Hernández^a

^a Grupo de Investigación en Física Aplicada, Departamento de Física, Universidad Del Norte, Barranquilla, Colombia

^b Centro Atómico, Bariloche, Argentina, 8400 S. C. de Bariloche, CONICET, Argentina

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ABSTRACT

Charged vacancy defects in an AlN nanosheet are studied by first principles calculations. Formation energies values at valence band maximum indicate that the nitrogen vacancy is more stable than the aluminum vacancy in both Al and N rich conditions. Under Al-rich and N-rich conditions, aluminum vacancy presents two transition levels in the band gap: from neutral state to a negative charge-state (0/−1), and from a negative charge-state to a double negative charged state (−1/−2). Nitrogen vacancy at low Fermi energies prefers a positive charged state, then it adopts a neutral charged state, and finally it is stabilized in a negative charge-state. Bond lengths of atoms in vicinity of vacancy and electronic structure are affected by charge states. AlN sheet with vacancy defects could present spin-polarized charge states. Magnetism originated by charged vacancy defects in AlN sheets can serve for potential applications in new spintronic devices.

1. Introduction

The remarkable electronic, magnetic and mechanical properties of graphene have sparked an intense research in two-dimensional materials (2D) during the last decade [1–9]. It is expected that these properties, which could offer novelty applications in new nanotechnologies, can be extended to honeycomb structures with III Nitride materials. In order to find similar physical features in these structures, recent studies on vacancy defects or adatoms have been carried out [10–15].

Among the III Nitride compounds, aluminum nitride (AlN) has been intensively studied in 3D because of the following physical features: it is a direct semiconductor with a large band gap (6.2 eV), high electrical resistivity, dielectric strength, high hardness, high thermal conductivity, low thermal expansion coefficient, high thermal stability, high value of surface acoustic wave velocity, and it exhibits oxidation and wear resistance [16–26]. These properties may be useful in the design and production of electro-optical devices operating under extreme conditions, and for wireless communication devices. Light-emitting diodes (LEDs), diode lasers (LDs), Ultraviolet light emitting diodes (UV-LEDs), Schottky diodes, and heterostructure field effect transistors (HFETs) are realizations on AlN substrates [27,28].

Moreover, a continued effort has been made to develop AlN-based device applications in low dimensionality. Several investigations of AlN nanowires have revealed excellent field emission, transport, photoluminescence, mechanical, thermal conductance, and piezoelectric

properties. These physical features have allowed many potential applications in the development of new generation electronic devices, such as the FETs, single-nanowire photodetector, gas sensors, and nanowire-based light emitting nanodevices [29–31]. Recently, 210 nm emitting AlN nanowire LEDs were achieved [32].

AlN honeycomb sheet was theoretically reported as a stable ionic monolayer [33]. Furthermore, the adsorption of CO₂ and N₂ molecules on AlN nanostructures was investigated. From the results of this study, the authors suggest applying aluminum nitride nanostructures for CO₂ capture and storage [34]. Ultrathin AlN nanosheets were grown epitaxially by plasma assisted molecular beam epitaxy on Ag(111) single crystals, showing a graphite-like hexagonal structure [35]. The formation of a graphene-like AlN layer on a (111)Si substrate by ammonia molecular beam epitaxy was studied [36].

A research field related to the study of mechanical and spintronic properties of AlN sheets with vacancy defects or adatoms and their heterostructures, has initiated [37–54]. It was shown that vacancy defects or adatoms on AlN sheet lead to significant changes in the band structure in the vicinity of the Fermi level. However, these studies do not consider charged defects. Motivated by this, we have carried out a detailed study on the effects of charged vacancy on formation stability, electronic structure and magnetic properties of AlN nanosheets. Therefore, in this work we have researched the formation energies and charge transition levels of charged Al-vacancy (V_{Al}) and N-vacancy (V_N) in AlN nanosheet, through total energy first-principles calculations

* Corresponding author.

E-mail address: wlopez@uninorte.edu.co (W. López-Pérez).

within the density functional theory (DFT) framework [55,56]. In addition, we made a special emphasis on effects of charged vacancies on AlN planar's electronic structures and magnetic properties.

2. Computational methods

In this work, the calculations were performed using the pseudo-potential method within the DFT formalism. Exchange and correlation effects were treated with generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) [57]. The core electrons were described by the projector augmented wave (PAW) method [58,59]. The calculations were performed using the Vienna ab initio simulation package (VASP) [60,61]. As starting point, a 1×1 unit cell consisting of a hexagonal layer of one Al and one N atom has been employed. To prevent spurious interactions between charged vacancies by finite-size effects, the local vacancy defect calculations in AlN monolayers were performed using 6×6 supercells. A vacuum region of $12 \text{ \AA}$ between neighboring sheets was considered along the $[0\ 0\ 0\ 1]$ direction to avoid interlayer interactions. Gamma-centered grids of $36 \times 36 \times 1$ and $6 \times 6 \times 1$ k-points were used to sample the irreducible Brillouin zone of the 1×1 and 6×6 systems respectively, in the Monkhorst-Pack special scheme [62]. The valence electron wave functions were expanded in a plane wave basis up to a cutoff energy of 460 eV. In order to determine the equilibrium geometry of AlN monolayer with vacancies, all the atomic coordinates are relaxed through the conjugate gradient algorithm, until an energy convergence of 10^{-6} eV and a force on each atom smaller than 10^{-4} eV/Å. Methfessel-Paxton smearing technique with a smearing width of 0.05 eV was adopted to set the partial occupancies for each orbital in the total energy calculations [63].

In this study, the vacancy formation energy calculations were performed using the formula given by Refs. [64–66]:

$$E_f[V^q] = E_{tot}[V^q] - E_{tot}[host] - \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q(E_{VBM} + E_F + \Delta V) + E_{MP} \quad (1)$$

where $E_{tot}[V^q]$ is the total energy for the supercell with vacancy defect at charged state q , $E_{tot}[host]$ is the total energy of the host supercell, n_{α} is the number of atoms type α subtracted from the monolayer, creating the vacancy defect; and μ_{α} is the chemical potential of the species α . Energy per atom of the face-centered cubic aluminum was used as the chemical potential of Al, and the energy per atom of the nitrogen molecule was computed as the chemical potential of N. E_{VBM} is the valence band maximum energy of the perfect monolayer, E_F is the Fermi energy level with respect to VBM, which is considered zero if it coincides with VBM, ΔV is the correction to the total energy due to electrostatic potential alignment for nanosheet with and without vacancy, and E_{MP} is the modified Makov-Payne correction for image charge [67–69] because our supercell is finite.

3. Results and discussion

3.1. Perfect AlN nanosheet

The first predictive study of the dynamic stability of a single-layer honeycomb of aluminum nitride has already been mentioned in the introduction section [33]. In order to study charged vacancies in this monolayer, first a structural optimization for graphite-like hexagonal crystal of AlN was performed. Our optimized lattice constants for h-AlN bulk are $a = 3.30 \text{ \AA}$ and $c = 4.15 \text{ \AA}$. In h-AlN bulk, the optimized Al–N bond length was of $1.90 \text{ \AA}$, and each Al–N bond is formed by $2.50 e^-$ charge transfer from an Al to N atom, allowing it to gain an ionic character. These results are in good agreement with the reported values in Ref. [48]. Next, the two-dimensional (2D) AlN nanosheet was constructed in a 6×6 supercell. This 2D-AlN monolayer contains 36 Al and 36 N atoms arranged in the xy plane. Both top and side views of the

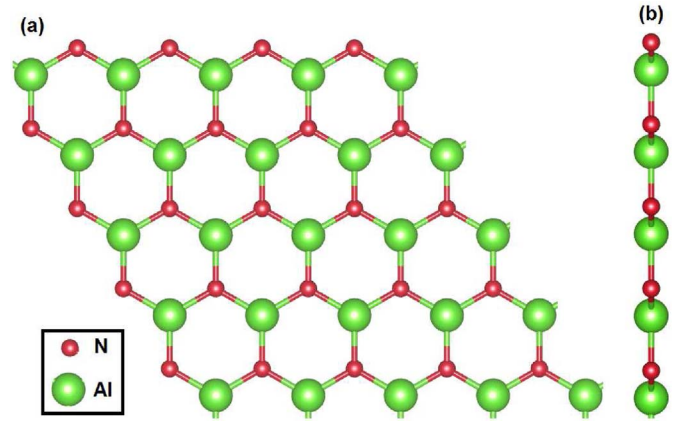


Fig. 1. Top(a) and side views (b) of the relaxed AlN nanosheet honeycomb structure.

optimized atomic structure of 2D-AlN nanosheet are shown in Fig. 1. This graphene-like honeycomb structure shows an Al–N bond length of $1.80 \text{ \AA}$, which is smaller than that of the AlN hexagonal bulk. This confirms that the sp^2 bonding in 2D honeycomb structure is stronger than the sp^3 bonding of bulk. The obtained lattice parameter for honeycomb hexagonal 2D-AlN was of $3.13 \text{ \AA}$, which is in excellent agreement with the value experimentally measured ($3.13 \text{ \AA}$ [35]).

Fig. 2 shows the band structure of the AlN perfect nanosheet calculated using GGA-PBE. A symmetrical behavior of the up and down spin curves of the band structure was observed, indicating that the perfect AlN nanosheet is nonmagnetic. The band structure shows that the AlN monolayer has a wide band-gap with 2.93 eV value, calculated by using GGA-PBE. Nevertheless, the hybrid HSE-06 functional [70] was used to correct the band-gap energy, leading to a value of 4.02 eV. These values are in very good agreement with those reported by Bakasiz et al. [48]. In the AlN nanosheet, the atoms of Al and N have $3s^2 3p^1$ and $2s^2 2p^3$ valence states, respectively, so two electrons from each N atom create a solitary pair in the perpendicular direction to the monolayer. Therefore, a sp^2 -hybridization is formed by the orbitals in AlN nanosheet, and has unoccupied p_z orbitals from Al atoms and solitary pairs of p_z electrons from N atoms. Thus, the valence bands are mainly originated from the N-2p states, while conduction bands would be mainly occupied by the Al-3p states.

3.2. Defect formation energies

To predict stability of charged vacancies in an AlN nanosheet, the

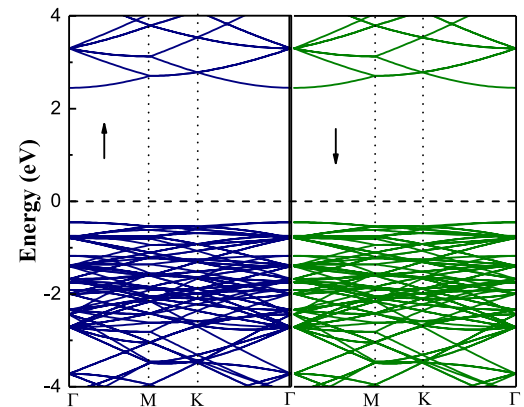


Fig. 2. Spin-dependent band structure for the pure AlN nanosheet, obtained by using GGA-PBE methods. Arrows indicate each spin orientation. Electronic band structure corresponding to spin up channel was drawn with blue color, while the green color was used for spin down orientation's one. The Fermi level is set to zero and marked out by the horizontal dashed line.

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