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Electronic structure of GaN nanotubes

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ABSTRACT

Nanotube properties are strongly dependent on their structures. In this study, gallium nitride nanotubes (GaNNTs) are analyzed in armchair and zigzag conformations. The wurtzite GaN (0001) surface is used to model the nanotubes. Geometry optimization is performed at the PM7 semiempirical level, and subsequent single-point energy calculations are carried out via Hartree–Fock and B3LYP methods, using the 6-311G basis set. Semiempirical and *ab initio* methods are used to obtain strain energy, charge distribution, dipole moment, |HOMO-LUMO| gap energy, density of states and orbital contribution. The gap energy of the armchair structure is 3.82 eV, whereas that of the zigzag structure is 3.92 eV, in agreement with experimental data.

1. Introduction

In recent years, nanotube materials have been intensely investigated due to their physical and chemical properties [1–9]. It is well known that these properties are strongly dependent on structural organization and also on the presence of vacancies and impurities [7,10–15]. Gallium nitride is an important material due to its optoelectronic properties and high thermal and mechanical stability, which is also appropriate to produce light-emitting diodes (LEDs) with short wavelengths [13,16–23]. Wurtzite is the thermodynamically stable phase of GaN, which is a semiconductor material and shows a band gap close to 3.4 eV [18,24–26].

GaN nanotube materials have attracted wide theoretical and experimental interest [20,27–33]. Hemmingsson et al. observed a band gap of 3.46 and 3.75 eV for GaNNTs [27]. Yang et al., using DFT, found a band gap of 1.72 eV for zigzag GaNNTs with 5.35 Å diameter [30]. They also showed that the band gap increases with the diameter size. The Ga 3d band was found at 19.9 eV of binding energy from PES spectra with a band gap of 3.37 eV [28]. However, the energy gap of small nanotubes is not well known, because this depends on structural organization [31]. Consequently, the study of nanotube geometry is important to better understand their electronic and magnetic properties [11,34–37].

Many methodologies have been used for building inorganic nanotube models, based on graphene [20,35,38] or on the crystalline structure [39,40]. In this work, we used cluster models to generate gallium nitride crystal coordinates in the wurtzite phase for the (0001) surface to obtain nanotubes in the armchair and zigzag conformations. The (0001) surface of GaN was used as it is the most studied termination [41–43].

1.1. Methodology

The lattice parameters of the GaN crystal in the wurtzite phase [44] were used to generate the coordinates of the

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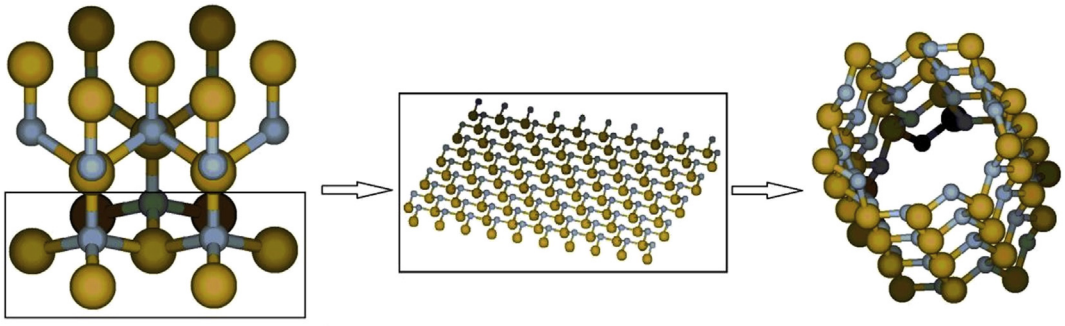

Fig. 1. GaN cell, (0001) surface and modeled nanotube. Large spheres represent Ga atoms, while small spheres represent N atoms.

(0001) surface, and the sheet was wrapped to form the nanotube (Fig. 1).

The nanotube geometry was fully optimized using the PM7 semiempirical method [45] as implemented on the MOPAC 2012 package [46]. PM7 shows small average errors compared to other semiempirical parametrizations [46]. The PM7 method was also used to calculate strain energy (E_s), energy variation (ΔE), charge distribution, dipole moment and orbital contribution.

$$E_s = \frac{E_{tube} - E_{plane}}{number\ of\ GaN\ units} \quad (1)$$

$$\Delta E = E_{(n,m)k} - k \cdot E_{(n,m)1} \quad (2)$$

where n and m are integers of the chiral vector (n,m) and k is the number of nanotube cluster layers, $n = m$ for armchair and $m = 0$ for zigzag.

Table 1
Strain energy (eV) for armchair $(5,5)_{10}$ and zigzag $(10,0)_{10}$ models.

	Armchair	Zigzag
PM7	−1.856	−1.732
HF/6-311G	−1.767	−1.578
B3LYP/6-311G	−1.695	−1.619

The optimized coordinates were used as the input for the single-point Hartree–Fock (HF) and B3LYP methods with the 6-311G basis set, to calculate the strain energy (Eq. (1)), energy variation (Eq. (2)), charge distribution, dipole moment and the frontier orbitals, and the difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital (|HOMO–LUMO|). First principles calculations were carried out using Gaussian 03 software [47].

2. Results and discussions

The strain energy (E_s) values are shown in Table 1. As expected, the analysis of nanotube stability, comparing the strain energy of nanotubes in both conformations, indicates that the nanotube structures are more stable than the isolated surface. The variation of energy due to the nanotube growth along the z-direction parallel to the surface (Fig. 2) has shown that the growth is directly proportional to the nanotube stability. The GaNNTs obtained experimentally indicated a length close to 1 μm [12].

Comparing the strain energy, we found a difference of −0.076 eV for the GaN unit (B3LYP/6-311G) between armchair and zigzag conformations. The armchair was found as the most stable conformation. However, it is possible to note the distortion in the extremities of this

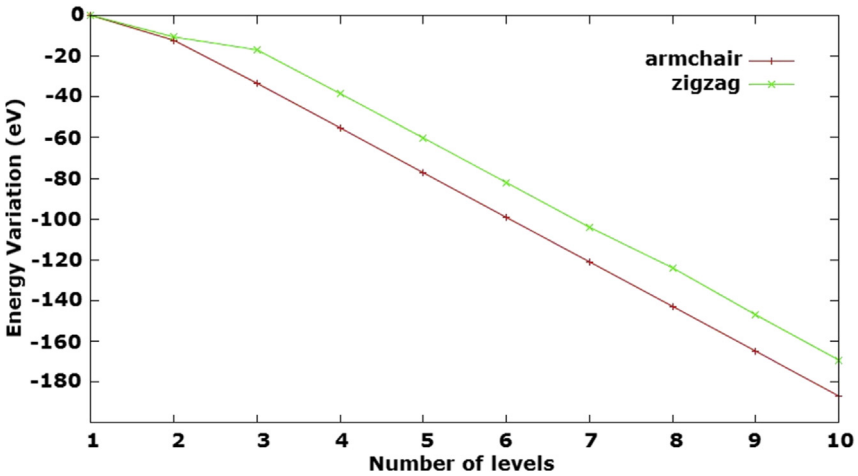

Fig. 2. Energy variation related to the nanotube growth for armchair (5,5) and zigzag (10,0) models.