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An ab initio study of the size-dependent mechanical behavior of single-walled AlN nanotubes

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ABSTRACT

Employing ab initio electronic structure calculations combined with the linear combination of atomic orbitals (LCAO) we have investigated a size dependence of mechanical behavior in single-walled AlN nanotubes with armchair and zigzag forms. A simple procedure of nanotubes construction based on the wurtzite (0 0 1) slab with monolayer rolling and subsequent cylindrical coordinate system introduction is suggested. The present calculations indicate that the Young's modulus and electronic band gap of these tubes are increased monotonically as the radius increases, but decreases with the Al—N bond length. In addition, the amount of charge transfer calculated by the Mulliken's population analysis is introduced to explain clearly the strength of bonding between Al and N atoms in single-walled AlN nanotubes.

1. Introduction

Presently, III-V semiconductor nanostructures materials [1,2] have attracted more attentions as they are expected to play an important role in the development of future nanoscale technologies. Currently, Aluminum nitride nanostructures (needles [3], platelets [4], nanowires [5–7], nanoribbons [8], and nanotubes [9,10]) have aroused considerable interest because of their novel properties as well as extreme different functionality compared to their bulk counterparts, such as enhanced field emission, high thermal conductivity, good dielectric properties, large electrical resistivity, large optical band gap, low thermal expansion coefficient. Most of all, AlN nanostructures have higher reactivity than carbon nanotubes or BN nannotubes due to their great polarity, which make AlN nanostructures be suitable for advanced nanoscale electronic and optoelectronic device applications. AlN nanostructures are not only used for field emitters in flat panel displays, potential hydrogen storage media [11] and integration compatibility with silicon substrates but also make them to be excellent candidates for actuators, sensors, and nano-electromechanical systems [12,13]. So the knowledge of the structure and properties of AlN nanostructures are required.

AlN nanotubes with diameters of 30–80 nm have been successfully synthesized via direct nitriding of aluminum powder [14–16], theoretical calculations on single-walled AlN nanotubes have indicated that these tubular structures are stable and have unique electronic properties [17–19]. Although AlN nanotubes have been extensively investigated over the past years, to the best of our knowledge, there are few first principle simulations about the elastic properties by a consideration of AlN nanotubes with different sizes and structures.

In this paper, we evaluated the strain energy required in order to wrap up an AlN graphitic sheet into a singled-walled AlN nanotube based on density functional theory (DFT) calculations. We found that the energy cost to form an AlN nanotube from its sheet structure is lower than that required to form carbon, GaN, and BN nanotubes from their corresponding graphitic materials. The electronic structures of armchair and zigzag AlN nanotubes with different radius have also been obtained by using DFT calculations. All the AlN nanotubes are predicted to be semiconductors with band gaps ranging from 5.37 to 7.78 eV. Their energy band gap slightly depends on the chirality, but significantly on the radius for the tubes of small radius. The zigzag and armchair nanotubes are both semiconductors with direct and indirect band gap, respectively. Contrary to the cases of carbon nanotubes, the band gap of AlN nanotubes increases with the increasing radius of the tubes and

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saturates at a value corresponding to the calculated band gap of an AlN hexagonal sheet. The existence of a direct gap in zigzag nanotubes is rather important, because it suggests that such nanostructures may exhibit a strong electroluminescence, which has never been observed for their bulk materials [20].

This paper is structured as follows: in Section 2 we describe our computational details. In Section 3 we discuss structures and energetic properties, the radius and chirality dependence of the elastic constants. And Section 4 contains the main conclusions.

2. Theoretical background

Aluminum nitride is the only stable compound in the group III nitrides and exists in only one crystal structure (wurtzite, hexagonal), which is described by the *P*63*mc* space group. Calculations were performed with the CRYSTAL06 periodic ab initio code [21], which using the formalism of localized Gaussian-type atomic orbitals and the nanotubes construction based on the two dimensional wurtzite (001) layer rolling and subsequent cylindrical coordinate system introduction is adopted.

Here we have considered two types of single-walled aluminum nitride nanotubes (SWAlNNTs), namely, armchair and zigzag, as shown in Fig. 1. The original structures of armchair type (n, n) and zigzag type (n, 0) SWAlNNTs are constructed by rolling up an AlN graphitic sheet. The exchange-correlation potential is according to the generalized gradient approximation (GGA) corrections in the form of PWGGA (Perdew–Wang generalized gradient approximation) [22–25] which has been applied to variety of problems in clusters, surfaces and solids. The all-valence basis sets for Al (8s511sp1d) [26] and N (81s31p1d) [27] GTFs were optimized elsewhere that have been used, therefore we only slightly have re-optimized their diffuse exponents of valence *s*, *p* and *d* orbitals in bulk wurtzite calculations with exchange-correlation DFT functional PWGGA. For accuracy, we have used the reciprocal space integration with the suitable shrinking factors for the Monkhorst–Pack and Gilat nets: 8 × 8 × 8, the level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series is controlled by five parameters, for which the 8 8 8 8 16 values were used. The SCF convergence on energy was set to 10^{-8} E_h ($1E_h = 27.2114$ eV).

The bulk wurtzite atomic and electronic structure was reproduced as $a = 3.083$ Å (3.11), $c = 4.850$ Å (4.98), $u = 0.384$ Å (0.382), and the band gap $E_g = 6.48$ eV (6.2 eV) which are in fair agreement with the experiments [28,29] (in brackets the experimental values are given). Our calculations were performed for (n, 0) zigzag (n ranging from 4 to 23) and (n, n) armchair (n from 4 to 23) AlN nanotubes as a function of n with radius (R) ranging between 2.08 and 19.37 Å.

3. Results and discussion

For the optimized SWAlNNTs, Al and N atoms shift inward and outward along the tube's radius so that all of the Al and N atoms are located at two different coaxial cylindrical surfaces (see Fig. 1) whose radius are denoted as R_{Al} and R_N.

R_{Al} and R_N are not equal in the same nanotube but very close, so a common radius has been defined as equation (1) to compare the properties of AlN nanotubes with different sizes and structures.

$$R = \frac{R_{Al} + R_N}{2} \tag{1}$$

The total energy of the optimized tubes was calculated as

$$E = \frac{E_{tot}(\text{unit cell of AlN model})}{n_{AlN}} \tag{2}$$

where E_{tot} is the calculated total energy per molecule or unit cell and n_{AlN} is the number of AlN pairs per unit cell. Fig. 2 shows the size dependence of the total energy for fully relaxed SWAlNNTs. It is seen that a strong size effect is evident for both types of tubes. By comparison of total energies, SWAlNNT of zigzag form is found to be more stable than that of armchair form. The total energies of armchair and zigzag NTs decrease monotonically with increased radius and tend to the AlN graphitic sheet when the radius is

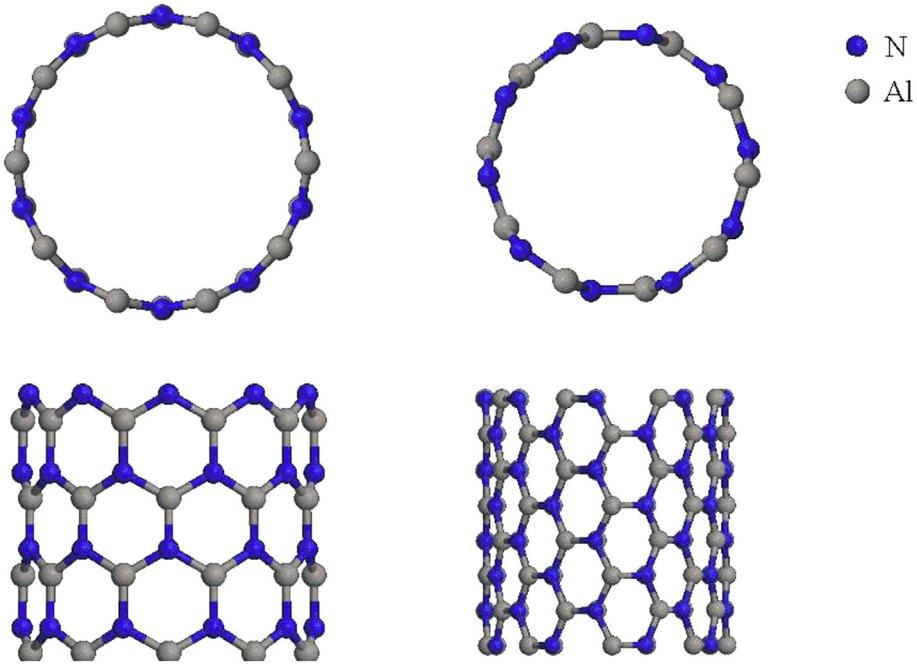

Fig. 1. The optimized zigzag (left) and armchair (right) AlN nanotubes.