

Stability and electronic structure of AlN nanotubes

Mingwen Zhao,^{1,*} Yueyuan Xia,¹ Dongju Zhang,² and Liangmo Mei¹

¹Department of Physics, Shandong University, Jinan 250100, China

²School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China

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We predict the stability and electronic structure of aluminum nitride nanotubes based on calculations using density functional theory. The lower strain energy required in order to wrap up an AlN graphitic sheet into a tube and good thermal stability indicate the possibility for the formation of AlN nanotubes. All the AlN nanotubes are semiconductors with band gaps ranging from 2.84 to 3.95 eV. The zigzag nanotube is a semiconductor with a direct band gap, whereas the armchair nanotube has an indirect band gap. Contrary to the cases of carbon nanotubes, the band gap of AlN nanotubes increases with the increasing diameter of the tubes and saturates at a value corresponding to the calculated band gap of an AlN hexagonal sheet.

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I. INTRODUCTION

Ever since the discovery of carbon nanotubes,¹ there have been significant research efforts to synthesize nanometer-scale tubular forms of various materials and to study their properties both experimentally and theoretically. Among these materials, III-V semiconductors, and the group-III nitrides, in particular, have attracted much attention due to their potential technological applications. Tubular forms of group-III nitrides have been variously predicted and observed in experiments.²⁻⁷ Cohen and coworkers predicted the existence of BN and BC₂N nanotubes² and the synthesis of double-walled boron nitride nanotubes have been achieved through various techniques including plasma-arc method.³ More recently, single-crystal gallium nitride nanotubes with inner diameters of 30–200 nm and a wall thickness of 5–50 nm have been synthesized.⁵ First-principles calculations of AlN nanotube (*h*-Al₂₇N₂₇) show that it possesses a uniform diameter and a larger band gap than a corresponding nanowire structure. The π orbital property of highest occupied molecular orbital of an AlN nanotube similar to that of carbon nanotube suggests the possibility of the formation of AlN nanotubes.⁶ However, the strain energies required to form nanotubes from their sheet structures, as well as their thermal stability, which are regarded as important data in predicting the existence of tubular structures,⁷ have not been reported up to now. Although in recent experiments, a tubular form of AlN with a diameter \sim 50 nm has been synthesized using a highly nonequilibrium dc-ac plasma method,⁸ the synthesis of single- or double-walled AlN nanotubes is still an open question.

Moreover, as is well known, the physical properties of carbon nanotubes are correlated with their diverse phases. Carbon nanotubes are always described by rolled graphene where a hexagonal two-dimensional lattice is mapped on a cylinder of radius R with various helicities characterized by a set of two integers (m, n). Theoretical studies have revealed that carbon nanotube is either metallic or semiconducting depending on its diameter and chirality.⁹⁻¹¹ Armchair (n, n) carbon nanotubes are metallic, while zigzag ($n, 0$) carbon nanotubes are semiconductors with a finite band gap except for the case of $n - m = 3k$ (k is an integer), which is a small

band gap semiconductor. This different behavior can be qualitatively explained in terms of the two-dimensional graphite band structure and discrete wave vectors allowed by boundary conditions in the tubes. However, different from graphite, group-III nitrides are wide-band-gap semiconductors. In particular, cubic AlN has a large band gap of 6.2 eV. Therefore, their corresponding tubular structures may show electronic properties quite different from those of carbon nanotubes. Previous theoretical investigations have revealed that both BN and GaN nanotubes are semiconductors,^{2,4} and their electronic properties depend slightly on chirality. However, to our knowledge, the dependence of the electronic properties, in particular the band structures, of AlN nanotubes on their chirality and diameter have not been reported so far. Considering the potential applications of AlN nanotubes, as field emitters, for example,⁸ theoretical studies on the electronic properties of AlN nanotubes with diverse phases are highly desirable.

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 (DF) calculations, and compared it to the results of BN, GaN, and carbon nanotubes. We found that the energy cost to form an AlN nanotube from its sheet structure is lower than that required to form BN, GaN, and carbon nanotubes from their corresponding graphitic materials. The electronic structures of armchair and zigzag AlN nanotubes with different diameters have also been obtained by using DF calculations. All the AlN nanotubes are predicted to be semiconductors with band gaps ranging from 2.84 to 3.95 eV. Their energy band gap slightly depends on the chirality, but significantly on the diameter for the tubes of small radius. Zigzag nanotube is a semiconductor with a direct band gap, whereas an armchair nanotube has an indirect band gap. 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.⁷

II. THEORETICAL APPROACHES AND COMPUTATIONS

We performed density functional calculations using an efficient *ab initio* code known as SIESTA.¹² This code is based

on the density functional theory adopting a localized linear combination of numerical atomic-orbital basis sets for the description of valance electrons and a norm-conserving non-local pseudopotential for the atomic core. The pseudopotentials were constructed using the Trouiller and Martins scheme¹³ to describe the valance electron interaction with the atomic core and the nonlocal components of the pseudopotential are expressed in the fully separable form of Kleiman and Bylander.^{14,15} The exchange-correlation potential is according to the generalized gradient approximation corrections in the form of Perdew, Burke and Ernzerhof,¹⁶ which has been applied to variety of problems in clusters, surfaces and solids. The atomic orbital basis set employed throughout the calculations was double- ζ plus polarization orbitals. The charge density was projected on a real space grid with an equivalent cutoff of 100 Ry to calculate the self-consistent Hamiltonian matrix elements. Periodical boundary condition along the tube axis was employed for AlN nanotubes with vacuum region (10 Å) between tubes. The supercell of the AlN nanotubes contains ten layers of atoms along the tube axis. In order to determine the equilibrium configurations of AlN nanotubes under study, we relaxed all the atomic coordinates with a conjugate gradient algorithm, reaching a tolerance in the force of $F_{\max} < 0.01$ eV/Å. Binding energies were calculated from the difference between the total energy of AlN nanotubes and the energies of the corresponding isolated Al and N atoms.

III. RESULTS AND DISCUSSION

We first determined the equilibrium configurations of different AlN nanotubes. The average Al—N bond length was calculated to be 1.83 Å, slightly shorter than that of zincblende (cubic) AlN, 1.89 Å.¹⁷ Similar to BN and GaN nanotubes,^{4,18} a slight distortion occurs in the wall of AlN tubes, where Al atoms moved toward the tube axis and N atoms moved in the opposite direction after relaxation, which made buckling. The radial buckling was 0.037 Å for (5,5) tube and 0.035 Å for (9,0) tubes. Comparing with those of BN and GaN tubes with similar diameters, the buckling in AlN nanotubes is the slightest.^{4,18} The larger the diameter the slighter the buckling will be. For (10,10) tubes, the buckling is only 0.018 Å. These bucklings are correlated with the slight different hybridizations of Al and N in the curved hexagonal layer. The surface dipoles resulting from these bucklings may be relevant to potential applications of these tubes. The thermal stability of AlN nanotubes has also been revealed in our first-principles molecular dynamics simulations. We simulated the annealing process of a (5,5) AlN nanotube at 1000 K for 2 ps, where the atoms in both ends are free to move. The tubular character was kept even at high temperature, and the buckling of the tube wall is very slight, as shown in Figs. 1(c) and 1(d). Due to the softness of the tube at high temperature, the cross section became ellipse [Fig. 1(d)]. This distortion caused by thermal motion can be recovered after reoptimizing. This clearly suggests the good thermal stability of AlN nanotubes. We also noticed that the atoms in both ends moved toward the tube axis, making the tube ends come close. Therefore, it can be expected that after being

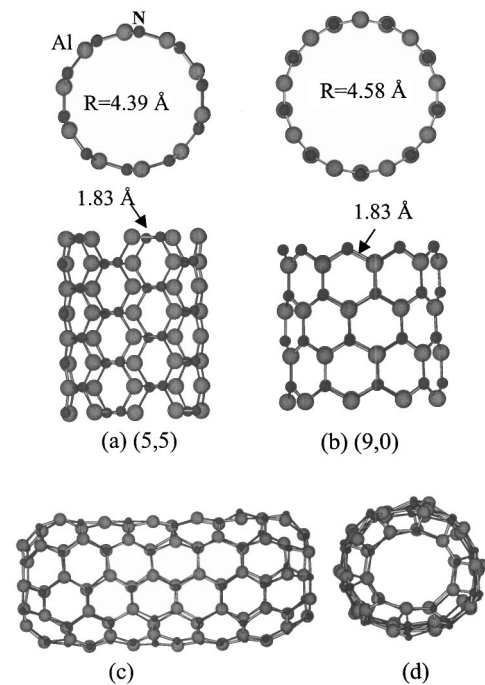


FIG. 1. The equilibrium structures of (a) (5,5) and (b) (9,0) AlN nanotubes. (c) and (d) The configuration of (5,5) AlN nanotubes after being annealed at 1000 K for 2 ps.

annealed at a higher temperature for a longer time, the AlN tube would become a close-ended tube, similar to the results found for BN nanotubes.²¹

In order to evaluate the strain energy required to wrap up a graphitic sheet into a tube, as well as the relative stability of AlN nanotube, we first calculated the binding energies of cubic and graphitic phases of AlN. A cubic supercell containing 64 atoms for zinc blende (cubic) AlN and 100 atoms for graphitic sheet were employed. Three- and two-dimensional periodic conditions were applied for cubic and graphitic phases of AlN, respectively. For the graphitic sheet, large vacuum region above the graphitic sheet was included. The binding energy of zinc blende AlN is -8.00 eV/atom with a nearest-neighbor distance of 1.90 Å, or equivalently a cubic lattice constant of 4.38 Å, in good agreement with other *ab initio* results.^{17,19} The binding energy of the graphitic sheet is -7.32 eV/atom with the nearest-neighbor distance of 1.83 Å. The energy difference between graphitic and zinc blende AlN of 0.68 eV/atom is higher than that between graphitic and zinc blende GaN, 0.36 eV/atom.⁴ The large difference in energy indicates that graphitic AlN structure is highly unstable, and can exit only under some extreme conditions.

Figure 2 gives the strain energy per atom required in order to wrap up an AlN graphitic sheet into an AlN tube of a given diameter, where the energy cost for the cases of BN, GaN, and carbon nanotubes are also presented for comparison. The strain energy decreases with the increasing diameter of the tube. Similar to the cases of BN (Ref. 19) and GaN (Ref. 4) nanotubes, the strain energies are relatively insensitive to the chirality of the tubes, in good contrast with the fact that carbon armchair nanotubes are more stable than zigzag nanotubes.²⁰ The strain energy is proportional to the

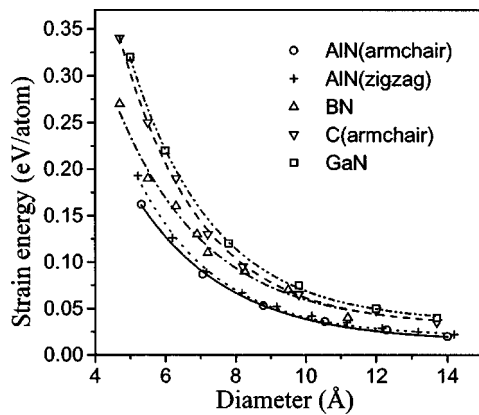


FIG. 2. Strain energy vs diameter for the formation of AlN armchair and zigzag nanotubes relative to their sheet structures. The strain energies of BN (Ref. 22), GaN (Ref. 4), and carbon nanotubes (Ref. 11) are also presented for comparison. The curves are fitted by the least-square method.

inverse square of the diameter, suggesting that AlN nanotubes follow classical elasticity theory. Although, experimentally, the growth mechanisms of AlN nanotubes are thought to have little to do with rolling the graphitic sheet up, the strain energies of AlN nanotubes relative to its graphitic sheet and cubic AlN materials are regarded as important references in predicting the existence of tubular structures. The lowest strain energy of AlN nanotubes relative to its graphitic sheet compared to those of carbon and BN tubes with a similar diameter seems to ensure the possibility for the synthesis of AlN nanotubes from a graphitic AlN sheet. However, considering the higher strain energy of a graphitic AlN sheet relative to cubic AlN (0.68 eV/atom), the synthesis of AlN nanotubes is still a higher challenge compared with that of BN, GaN, and carbon nanotubes.

The band structures along the tube axis and the corresponding density of states of a (5,5) AlN armchair nanotube and a (9,0) AlN zigzag nanotube are shown in Fig. 3. The

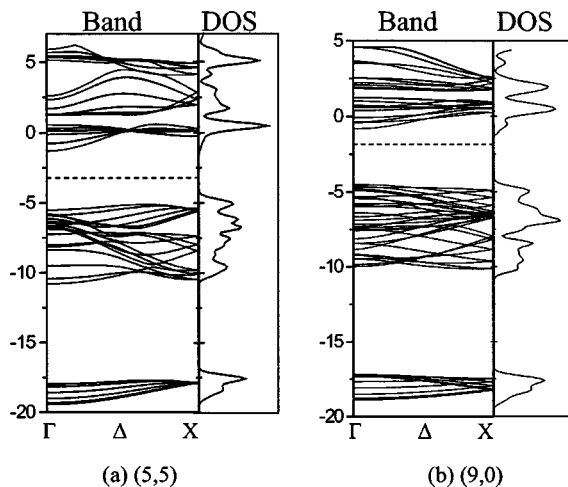


FIG. 3. Band structures along the tube axis and the corresponding density of states of (a) (5,5) the AlN armchair nanotube and (b) the (9,0) AlN zigzag nanotube. The armchair tube has an indirect gap (Δ - Γ) whereas the zigzag tube is direct (Γ - Γ).

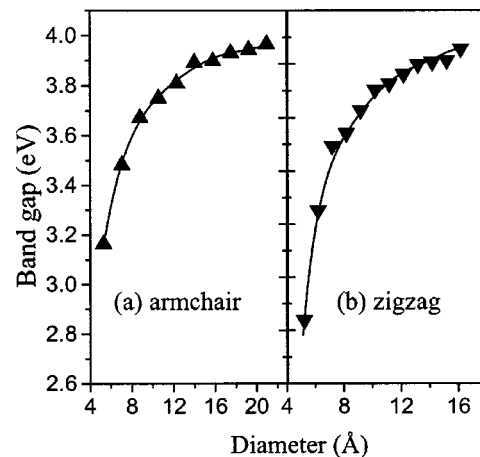


FIG. 4. Dependence of band gap of (a) armchair and (b) zigzag AlN nanotubes as a function of the diameter of the tubes.

supercell containing two layers (20 atoms) with the diameter of 8.79 Å was employed for (5,5) tube, while four layers (36 atoms) were included in the supercell of (9,0) tube with the diameter of 9.19 Å. Both (5,5) and (9,0) tubes are semiconductors with respective band gaps of 3.67 and 3.63 eV, quite different from the characters of carbon nanotubes where (5,5) and (9,0) are both metallic. This is related to the higher ionicity of AlN leading to the opening of a band gap in the hexagonal structure compared to semimetallic graphite. It is very interesting to see the differences in the band structures of armchair and zigzag nanotubes. Zigzag nanotubes have a direct band gap (Γ - Γ), whereas armchair nanotubes have an indirect band gap (Δ - Γ). The valence-band maximum of the armchair nanotube is near the middle of the Brillouin zone (Δ). We also found that zinc blende AlN shows an indirect band gap, in good agreement with the previous first-principles calculations.¹⁹ The existence of a direct gap in zigzag nanotubes is rather important, since it suggests that such nanostructures may exhibit strong electroluminescence, which has never been observed for the bulk materials.⁷

We also investigated the diameter dependence of the band gap for armchair and zigzag AlN nanotubes. The evolution of the band gap as a function of diameter of the tubes is given in Fig. 4. In the calculations of carbon nanotubes, all the armchair tubes are metallic, whereas the zigzag tubes oscillate between the metals and small- to medium-gap semiconductors. However, the band gap of AlN nanotubes increases monotonically with increasing diameter, and saturates at the calculated gap for graphitic sheet of AlN. This is quite similar to the result found for hexagonal AlN where the band gap decreases as the external pressure increases.¹⁹ This may be related to the strain in the AlN nanotubes which affects the hybridizations of Al and N and in turn modifies the band gap of the tube. The strain energy in the AlN nanotube increases, and consequently the band gap shrinks as the nanotube diameter becomes smaller. The sensitivity of energy band gap to the strain suggests the potential application of AlN nanotubes as interesting piezoelectric materials.

IV. CONCLUSIONS

Our calculations show that the strain energy required in order to wrap up a graphitic sheet into an AlN nanotube is

lower than those to form BN, GaN, and carbon nanotubes with the similar diameter, whereas the energy difference between graphitic and zinc blende AlN is high. All the AlN nanotubes are found to be semiconductors with band gaps ranging from 2.84 to 3.95 eV. The zigzag nanotube is a semiconductor with a direct band gap, whereas the armchair nanotube has an indirect band gap. The band gap of AlN nanotubes increases with the increasing diameter of the tubes.

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*Corresponding author. Email: zmw@sdu.edu.cn

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