The Ultra-Small Armchair Boron Nitride Nanotubes Study Using a Density Functional Theory Method.

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Abstract. A density functional theory (DFT) method was used to study the structures, stability and band gaps of the ultra-small armchair boron nitride nanotubes (BNNTs). We define the ultra-small size of the armchair boron nitride nanotubes (BNNTs) as a nanotube with diameter less than 1 nm. Each armchair nanotube’s stability and band gap was obtained by varying the size of nanotube diameters up to 1 nm. The larger size of diameter the higher stability and wider armchair nanotubes band gap. The results of the ultra-small armchair calculation confirm the same trend of properties with the available calculation data of ultra-small zigzag boron nitride nanotubes (BNNTs).

Keywords: density functional theory (DFT), ultra-small armchair boron nitride nanotubes (BNNTs), armchair structures, stability, band gap

1. Introduction

Boron nitride nanotubes (BNNTs) are predicted to be semiconductors regardless of the diameter, the chirality, and the number of tube walls [1, 2]. Because of these contrary properties to carbon nanotube (CNT), the homogeneity makes pure BNNT become a great promise material for device application[3]. However, not all pristine BNNTs are considered appropriate for electronic components even though they have the ability to be applied to nanotechnology[4]. Therefore, we attempt to point out the ultra-small BNNT, which has the chance to be used in different areas, but still has little attention to study.

Some literatures stated that the band gap of the zigzag BNNT would decrease rapidly with decreasing diameter when the diameter of those zigzag is less than 0.95 nm[4]. The curvature effect is expected to be a reason of this condition as shown by tight-binding[1] and first-principle calculation[3]. In previous study, we had calculated structural, stability, and electronic properties the (3, 0) zigzag up to (10, 0) zigzag BNNTs [5, 6]. There are correlations among structural geometry, stability and electronic properties in the ultra-small zigzag BNNTs. Herein, in this paper, we are interested to study the ultra-small armchair BNNTs if they have the same tendency with the ultra-small zigzag BNNTs.

In this paper, we perform a local density approximation (LDA) in density functional theory (DFT) is a method of study on ultra-small armchair BNNTs. The structural geometry optimization, stability, and band structure of each nanotube are investigated. We represent our computational details in Sec. 2, and our results and discussions in Sec. 3, respectively. Finally, a conclusion is given in Sec. 4.
2. Computational Details

In this paper, the first-principle calculations of the density functional theory (DFT) were carried out using the Vienna ab-initio simulation package [6–9]. The local density approximation (LDA) [10] and the ultra-soft pseudopotentials [11, 12] were used as an exchange correlation energy and ion-electron interactions, respectively. We used 450 eV cutoff and 1x1x16 k-point mesh for structural relaxation, and the calculation will be converged up to $10^{-6}$ eV and $10^{-2}$ eV for the energy differences and Hellman Feynman forces, respectively.

We used the hexagonal Boron Nitride (h-BN) where the basis vectors are $\vec{a}_1$ and $\vec{a}_2$ ($\vec{a}_1 = \vec{a}_2 = \vec{a}_0 = 0.2490 \text{ nm}$) separated with an inter-angle of 45° for (6, 6) armchair BNNT as shown in Figure 1. The chirality index on the hexagonal boron nitride (h-BN) sheet $(n, m)$ and the axial periodicity $(c)$ specify the circumference of BNNT. Therefore, a (6, 6) armchair BNNT is formed when a rectangle with sides $A$ and $c$ is cut out of h-BN and is then rolled up about the tube axis $c$ which perpendicular to the $A$ as illustrated in Figure 2. As shown in Figure 2, $r_1$ and $r_2$ were defined as bonds around the tube axis and bonds along the tube axis, respectively. Also, the diameters of both boron ($d_1$) and nitrogen rings ($d_2$).

We not only constructed (6, 6) armchair BNNT but also other chiral structures of BNNT starts from (2, 2) armchair up to (10,10) armchair BNNT. We displayed structural data of each nanotube as served in Table 1.
Then, stability of armchair BNNTs is defined by the average binding energy ($E_b$) which is calculated by the following formulas:

$$E_{b,\text{armchair}} = E_{h-BN} - E_n [BN(n, n)/2n]$$

where $E_{b,\text{armchair}}$, $E_{h-BN}$, $E_n [BN(n, 0)/2n]$, $E_n [BN(n, n)/2n]$ corresponds to the average of binding energy binding of armchair BNNT, the total energy of h-BN per atom, the total energy of zigzag BNNTs per atom, and the total energy of armchair BNNTs per atom, respectively.

In addition, the electronic properties of BNNTs were analyzed from the electronic density of state (DOS) and the band structure calculations.

3. Results and Discussions

We calculated ($n$, $m$) armchair BNNT ranging from (2, 2) up to (10, 10). We summarize our structural calculation results and other structural calculation results from a number of references as shown in Table 1. We also display the structural information of zigzag BNNT. One of the structural information of zigzag BNNT is taken from our previous calculation which had published. From the listed data as displayed in Table 1, we state that our BNNT structures is not a perfect cylinder since we find the B-N bond length ($r_2$) along tube axis is longer than the B-N bond length ($r_1$) around the tube axis ($r_2 > r_1$) particularly for the armchair structures. Moreover, the data also indicate that the diameters of nitrogen rings ($d_2$) is longer than the diameter nitrogen rings ($d_2$). Those differences can be tolerated since the diameter of our BNNT is small.

The structural property is related to the stability. The stability of our zigzag BNNT structures is achieved by calculating the binding energy as described before in computational details section. As a comparison, we also display the binding energy of the zigzag BNNT structures from our previously published calculation[5] as shown in Figure 3. From this figure, the larger BNNT diameter the higher stability of nanotube. We get the similar trend for both armchair and zigzag structures. So, we conclude that (10, 10) is the most stable structure among the others.
Table 1. Structural Parameters of BNNT (nm and eV). (\textsuperscript{a}Ref. [13], \textsuperscript{b}Ref. [14], and \textsuperscript{c}Ref. [5])

| Tubes | \( r_1 \) | \( r_2 \) | \( d_1 \) | \( d_2 \) |
|-------|--------|--------|--------|--------|
| \( (3,0) \) | 0.1445\textsuperscript{c} 0.1416\textsuperscript{a} | 0.1516\textsuperscript{c} 0.1508\textsuperscript{a} | 0.2748\textsuperscript{c} | 0.2749\textsuperscript{c} |
| \( (4,0) \) | 0.1439\textsuperscript{c} 0.1423\textsuperscript{a} | 0.1479\textsuperscript{c} 0.1476\textsuperscript{a} | 0.3220\textsuperscript{c} | 0.3504\textsuperscript{c} |
| \( (5,0) \) | 0.1437\textsuperscript{c} 0.1429\textsuperscript{a} | 0.1461\textsuperscript{c} 0.1460\textsuperscript{a} | 0.4167\textsuperscript{c} | 0.4168\textsuperscript{c} |
| \( (6,0) \) | 0.1436\textsuperscript{c} 0.1431\textsuperscript{a} | 0.1453\textsuperscript{c} 0.1452\textsuperscript{a} | 0.4777\textsuperscript{c} | 0.4960\textsuperscript{c} |
| \( (7,0) \) | 0.1435\textsuperscript{c} 0.1433\textsuperscript{a} | 0.1448\textsuperscript{c} 0.1448\textsuperscript{a} | 0.5688\textsuperscript{c} | 0.5688\textsuperscript{c} |
| \( (8,0) \) | 0.1435\textsuperscript{c} 0.1434\textsuperscript{a} | 0.1455\textsuperscript{c} 0.1455\textsuperscript{a} | 0.6357\textsuperscript{c} | 0.6489\textsuperscript{c} |
| \( (9,0) \) | 0.1435\textsuperscript{c} 0.1434\textsuperscript{a} | 0.1443\textsuperscript{c} 0.1443\textsuperscript{a} | 0.7241\textsuperscript{c} | 0.7241\textsuperscript{c} |
| \( (10,0) \) | 0.1435\textsuperscript{c} 0.1435\textsuperscript{a} | 0.1443\textsuperscript{c} 0.1443\textsuperscript{a} | 0.7943\textsuperscript{c} | 0.8046\textsuperscript{c} |
| \( (2,2) \) | 0.1460 0.1464\textsuperscript{a} | 0.1479 0.1465\textsuperscript{a} | 0.2672 0.2685\textsuperscript{a} | 0.3039 0.3057\textsuperscript{a} |
| \( (3,3) \) | 0.1442 0.1444\textsuperscript{a} | 0.1473 0.1450\textsuperscript{a} | 0.4257 0.4089\textsuperscript{a} | 0.4474 0.4318\textsuperscript{a} |
| \( (4,4) \) | 0.1440 0.1440\textsuperscript{a} | 0.1469 0.1444\textsuperscript{a} | 0.5437 0.5472\textsuperscript{a} | 0.5596 0.5639\textsuperscript{a} |
| \( (5,5) \) | 0.1439 0.1439\textsuperscript{a} | 0.1467 0.1442\textsuperscript{a} | 0.6927 0.6852\textsuperscript{a} | 0.7047 0.6975\textsuperscript{a} |
| \( (6,6) \) | 0.1439 0.1439\textsuperscript{a} 0.1441\textsuperscript{b} | 0.1466 0.1440\textsuperscript{a} 0.1440\textsuperscript{b} | 0.8726 0.8235\textsuperscript{a} | 0.8272 0.8336\textsuperscript{a} |
| \( (7,7) \) | 0.1439 0.1438\textsuperscript{a} | 0.1465 0.1439\textsuperscript{a} | 0.9622 0.9598\textsuperscript{a} | 0.9706 0.9683\textsuperscript{a} |
| \( (8,8) \) | 0.1438 0.1439\textsuperscript{a} 0.1441\textsuperscript{b} | 0.1465 0.1439\textsuperscript{a} 0.1442\textsuperscript{b} | 1.0900 1.0970\textsuperscript{a} | 1.0972 1.1045\textsuperscript{a} |
| \( (9,9) \) | 0.1438 0.1439\textsuperscript{a} 0.1439\textsuperscript{b} | 0.1465 0.1439\textsuperscript{a} 0.1441\textsuperscript{b} | 1.2331 1.2392\textsuperscript{a} | 1.2394 1.2457\textsuperscript{a} |
| \( (10,10) \) | 0.1438 0.1437\textsuperscript{a} 0.1437\textsuperscript{b} | 0.1464 0.1438\textsuperscript{a} 0.1438\textsuperscript{b} | 1.3626 1.3714\textsuperscript{a} | 1.3683 1.3772\textsuperscript{a} |

Figure 3. Binding energy vs. BNNT diameter (the zigzag BNNT binding energy data are taken from ref. [5])
The (10, 10) armchair BNNT is not only the most stable nanotube but also the structure which has the widest band gap among the others as depicted in Figure 4. However, it starts from (7, 7) armchair up to (10, 10) armchair BNNT, the differences of the band gap cannot be significantly observed (almost similar). When we look into their structural diameter, the diameter size of those nanotubes is larger than 9.5 nm. However, the other nanotubes which has diameter less than 9.5 nm, their band gap ranging down with the decrease of diameter size. That trend is applicable for both zigzag and armchair BNNT structures.

In order to explain the band gap of small armchair BNNT structures (d < 9.5 nm) decreasing with the declining of diameter size, we display the band structure of each nanotube as shown in Figure 6. The band structure of (2, 2), (3, 3), . . . , (6, 6) armchair are served in Figure 6 (a), Figure 6 (b), . . . , Figure 6 (e), respectively. From those figures, when we look at the band structures from Figure 6 (a) to Figure 6 (e), we conclude that the increasing diameter will move the valences band down or remain away to the conduction bands (the band gap would be open). Or, if we turn it over with other words, the decrease in nanotube’s diameter will move the valence band closer to the conduction bands.

However, there are no band movements around Fermi for both valence and conduction bands from Figure 6 (f) to Figure 6 (i). Thus, from Figure 6 (f) to Figure 6 (i), the (7, 7), (8, 8), (9, 9) and (10, 10) armchair BNNT, the width of the band gap is similar. Because of this, BNNTs known as insulator regardless of their size. In addition, The outcomes in this work inform us that BNNTs with diameter < 9.5 nm do not have common electronic properties like the BNNTs with diameter > 9.5 nm. By knowing the unique properties of BNNTs, BNNTs can be utilized in a variety of life applications.
Figure 5. Band structure of armchair BNNT. (a) (2,2) (b) (3,3) (c) (4,4) (d) (5,5) (e) (6,6) (f) (7,7) (g) (8,8) (h) (9,9) and (i) (10,10). The grey area indicates the band gap.

4. Conclusions

In summary, the ultra-small armchair BNNTs with the ultra-small zigzag BNNTs have the same tendency. The larger the diameter of nanotubes generates higher stability and wider nanotube band gap, as happened to the ultra-small zigzag BNNTs structures. Those structural, stability and the electronic properties of the ultra-small armchair boron nitride nanotubes (BNNTs) had been calculated using a density functional theory (DFT) method. Then, we found that the (10, 10) armchair BNNT not only is the most stable nanotube among other ultra-small armchair structures, but also the (10,10) armchair BNNT has the widest band gap among the others. It means that the BNNTs with diameter is larger than the diameter of the (10,10) armchair BNNT, will be more stable. However, the band gap of those BNNTs will be regardless of their diameter. Finally, the calculation outcomes of this work, hopefully may give a contribution to add literature and references for further research of BNNTs.
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