Superlattices and Microstructures 92 (2016) 198–209

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

The structure evolution process and the electronic properties of armchair boron nitride nanotubes

Chengpeng Yao, Yuchao Tang, Denghui Liu, Hengjiang Zhu*

College of Physics and Electronic Engineering, Xinjiang Normal University, Urumqi, PR China

ARTICLE INFO

Article history:
Received 20 January 2016
Received in revised form 31 January 2016
Accepted 1 February 2016
Available online 4 February 2016

Keywords:
BN tubular clusters
BNNTs
Geometry structure
Stability
Electronic property

ABSTRACT

We report the results of density functional calculations on the structural evolution and electronic properties of armchair boron nitride nanotubes (BNNTs), including SWBNNTs and DWBNNTs. Our results show that the initial structural configuration of the BNNTs was determined by the small boron nitride clusters. The evolution process of the BNNTs is through forming tubular clusters with a global reconstruction from structure of the double-rings. Then, it elongates through the layer-by-layer growth process with local reconstructions. Eventually, the infinite BNNTs can be constructed with corresponding repeat unit, designed by the periodic characteristics on the basis of tubular clusters. From the band structure of armchair BNNTs, it can be found the gap slightly increases with increasing diameter of the tube, decrease with the increasing of the walls. Moreover, the evolution process provides a better way to understand the growth mechanism of armchair BNNTs in atomic-level and guide the production of armchair BNNTs in industrial.

1. Introduction

BNNTs are always electrical insulators with a large band gap of about 5.9 eV [1,2], that is nearly independent to the tube diameter, chirality [3]. Boron nitride nanotubes (BNNTs) were theoretically predicted in 1994 by Rubio et al. [4,5] and experimental realization in the following year [6]. At present, many experimental and theoretical works have been done on the BNNT [7–19]. Properties of CNTs and BNNTs are different because the B-N bond is ionic [20]. BNNTs exhibit higher thermal and chemical stabilities compared to CNTs [21,22] and BNNTs show piezoelectric properties and a nonlinear optical response. BNNTs are expected to be used as electrical insulation coatings for conducting or semiconducting nanochains, nanowires, and nanotubes in high temperatures. BNNTs have many applications in the composite material, hydrogen storage, and force sensors [23–26]. BNNTs have better ability to store hydrogen compared to CNTs [27].

BNNTs are synthesized using a number of methods including arc-discharge [6], laser ablation [28], carbon substitution reactions [29], chemical vapor deposition [30] and ball milling and annealing methods [31–38] and so on. Although BNNTs can be synthesized by many ways, while the question of BNNTs structure and growth mechanism is no clear understanding. One of the reasons for this question is the lack of detailed knowledge about the tube atomic structure [39]. Therefore, a thorough understanding of the growth process from atomic-level is crucial to the preparation of BNNTs in the experimental.

* Corresponding author.
E-mail addresses: cpyao1990@yahoo.com (C. Yao), zhj@xjnu.edu.cn (H. Zhu).

http://dx.doi.org/10.1016/j.spmi.2016.02.002
0749-6036/

There are very little theoretical information of tube atomic structure has been given so far. In 1998, X. Blase reported it is due to the difference in electro negativity of B and N, the B–N bonds are partially ionic, in contrast with the purely covalent C–C bonds in graphitic structures. This effect can lead to the so-called lip–lip interactions between neighboring layers in BN nanosheets, which is why the formation of multilayer stabilizes the structure [40]. In fact, back in 1962 Blakely, J. M. and Jackson, K. A proposed the theory of nucleation [41] and experimental realization of multi-walled BNNTs (MWBNNTs) as guided by the theory of nucleation in 2008 [42]. It is noteworthy the BNO clusters are responsible for the growth of BNNTs [43]. Moreover, successful attempts to synthesize nanosized structures from boron nitride molecules [44–49] and the development of procedures for the synthesis of pure boron-nitride nanotubes [45]. while the nucleation theory does not provide information about the nucleus (BN tubular clusters) and growth mechanism of the BNNTs. In this works, we thus explored and obtained the structure and morphology of BNNTs nucleus and investigated the evolution process of armchair BNNTs from the nucleus, where such a process provides a better way to understand the growth mechanism.

In this paper, we investigated the evolution process of armchair BNNTs from nucleus (BN tubular clusters) using first principle DFT. The present paper is organized as follows. In Section 2, we briefly mention the computational methods. In Section 3, a detailed study for the evolution process of SWBNNTs and DWBNNTs from the BN tubular clusters with layer by layer growth is discussed. Our calculated results provides a better way to understand the growth mechanism of armchair BNNTs at the atomic-level. Section 4 concludes the present study.

2. Computational methods and detail

In this paper, the geometry optimization and the electronic structure calculations of the single-, double-walled BN tubular clusters, and the corresponding infinite BNNTs were performed using the DFT implemented in the GAUSSIAN03 package [50]. In particular, the hybrid Becke's 3-parameter and the Lee-Yang-Parr (B3LYP) function [51,52] were employed to describe the exchange-correlation potential. To better describe the geometrical features and the electronic structures of the BN tubular clusters and the BNNTs, the 3–21G basis sets have been chosen [53], which has been widely used [54–61] in the calculations of BN molecular electronic structures and energies. The calculated result of BN bond length is about 1.45 Å, in accordance with previously reported values [62]. It suggest that the method used in the present calculations is suitable for describing the behavior of BNNTs. The optimization was based on the energy system convergence, and the convergence of energy was better than 10^{-6} a.u.. To save time and improve the efficiency, the optimization process was divided into two steps. The first step was to optimize the structure with the prescribed bond length, bond angle, and dihedral angle of the initial values in the convergence criterion of 10^{-4} a.u.. The second step was to optimize the structure of BN tubular cluster by using the result of the first step in the convergence criterion of 10^{-6} a.u..

Based on the optimized BN tubular clusters, the unit cell of the infinite BNNTs were built by removing some atoms at the two ends of the structures. All of the unit cells of the infinite single- and double-walled BNNTs contain four layers of boron nitride atoms along the tube axis (taken as the x axis). We used the gradient-corrected correlation functional PBEPBE [63] (functional of Perdew, Burke and Ernzerhof) with periodic boundary conditions (PBC) [64] with the 3-21G basis sets for the structural optimization and band structure calculations of the infinite single- and multi-walled armchair BNNTs. The PBC model is based on the Gaussian type orbitals (GTOs) [65] that are transformed "crystalline orbitals (CO)" by employing the Bloch function [66]. Calculation of density of states(DOS) is based on the output coefficient matrix of wave functions and the discrete peaks were broadened using Gaussian functions with a broadening parameter of 0.5 eV. Then, the 241 k-points are used in all band gap calculations for the infinite single- and double-walled armchair BNNTs.

3. Results and discussion

In this section, we explored the evolution process of the SWBNNTs and DWBNNTs from the corresponding BN tubular clusters, by which we obtained their geometry and electronic properties. Meanwhile, the single-, double-walled BN tubular clusters are represented as $[p, k]$ and $[p, k]@[2p, k+2]$ respectively, where p is the number of atoms for each layer (determines the diameter) and k is the number of atomic layers (determines the length). Similarly, the SWBNNTs and DWBNNTs are represented as (n, n) and (n, n)@(2n, 2n) respectively, where $p = 2n$ (n = 3,4,5,6,8,10).

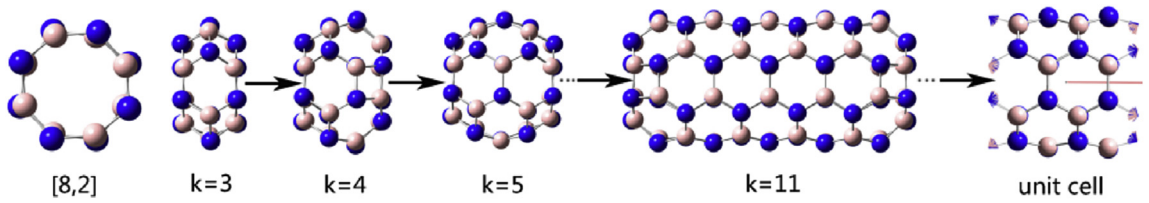

Fig. 1. Initial configurations, evolution process of [p, k] (p = 8; k = 2,3,4, …, 11) single-walled boron nitride tubular clusters and (4,4) BNNT.