Mechanical and emission properties of thinnest stable bamboo-like nanotubes

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Abstract. We investigate the stability of carbon bamboo-like nanotubes (BCNTs) with different diameters. It is shown that BCNTs with a diameter of 2.024 nm are the most stable bamboo-like nanotubes with the smallest diameter. It is shown that bamboo-like nanotubes with a certain distance between the bridges have superior emission properties than that the hollow nanotubes. Emission properties of the infinite bamboo-like nanotubes can be improved by adding the potassium atoms into the nanotube atomic structure. In this case the potassium atoms concentration should exceed 0.59%.

1. Introduction

Carbon bamboo-like nanotubes (BCNTs) find applications in various fields of science and technology due to their unique properties. In particular, bamboo-like nanostructures can be used as nanoindentors [1] to study the mechanical properties of the material, as well as nanoemitters in electronics [2].

Modeling of various properties of bamboo-like nanotubes has a large importance in the boundaries expansion of nanostructures application fields. Theoretical studies of electronic structure and topology of the atomic framework are carried out in order to identify the optimal configuration of bamboo-like nanotubes for a particular application scope.

It was found that the bamboo-like nanotubes have the improved mechanical properties compared to the hollow ones. It was experimentally established that the Young's modulus of bamboo-like nanotubes with a diameter of 10-20 nm and a length of 5-20 mm is equal to $4.5 \pm 0.8$ GPa, and tensile strength of the tubes with indicated geometric characteristics equals to $150 \pm 35$ MPa [3]. As a result of calculations performed in [4], it was found that the Young's modulus of nanotubes with a diameter of 10-45 nm and length of 1-20 mm is equal to $5.2 \pm 0.7$ GPa.

Currently, researches were conducted in the direction of reducing the work function of carbon tubular structures. It was found that the alkali metal atoms in nanotubes structure help to increase the emission current from the surface of nanotubes and to shift their current-voltage characteristic towards lower voltages [5-8].

Researchers' attention has been focused recently on the nanotubes of complex shape in order to improve the emissivity of carbon nanostructures. It was established that the current density of bamboo-like nanotubes with a diameter of 50-100 nm in the absence of doping with alkali metal atoms reaches saturation ($10^{-4}$ A/cm$^2$) at a field strength 4 V/mm [9].

The aim of this paper is a theoretical study of mechanical and emission properties of bamboo-like nanotubes. Investigation of mechanical properties was carried out for BCNT based on carbon nanotubes (CNT) (15,15) having a diameter of 2.024 nm and a length of 3.6 nm, and the CNT (10,10) having a diameter of 1.36 nm and a length of 3.728 nm. The study of the electronic properties was carried out for an infinite BCNT. We look for the stable configuration of BCNT using the tight-binding method [10]. Critical stress was found using the scheme presented in [11]. The modeling of the compression/expansion was carried out by empirical REBO method [12].

2. Modeling of the bamboo-like nanotubes and their geometrical parameters.

Bamboo-like structures were modeled by connecting fullerene fragments (bridge) to the inner surface of the hollow nanotube with the help of chemical bonds. The fragments of fullerenes $C_{250}$ and $C_{540}$ were used as bridges for the bamboo-like nanotubes constructed on the basis of the armchair nanotubes (10,10) and (15,15), respectively.

2.1. Study of the bamboo-like nanotubes stability

We look for the stable configuration of BCNT utilizing the optimization of atomic structure (i.e., minimization of the structure’s total energy by the atoms coordinates). It was established that the length of chemical bond equals to 0.16 nm for bamboo-like nanotube with a diameter of 1.36 nm and the length of the chemical bond equals to 0.14 nm for the bamboo-like nanotube with a diameter of 2.024 nm. Thus, BCNT with the diameter of 1.36 are metastable.
The detailed study of the fracturing process and predicting of the areas of possible chemical bonds break was based on analysis of the local atomic stresses distribution. Calculation of local stresses was performed according to the scheme presented in [11]. The calculations revealed that bamboo-like nanotubes with a diameter of 2.024nm are stable nanotubes of the smallest diameter. The critical stresses, at which the destruction of bamboo-like nanotubes begins, are approximately 11 GPa. The greatest value of the stresses experienced by the atoms of BCNT with a diameter of 2.024nm was 8.77 GPa. Therefore, the further study of the emission and mechanical properties (tensile/compression) of bamboo-like nanostructures will be applied to the model of BCNT with a diameter of 2.024nm due to the stability of its atomic structure.

2.2. Modeling of tension and compression bamboo-like nanotubes

In this paper the search for the critical tensile strength for BCNT (15.15) and hollow nanotubes was carried out. The modeling of the compression/expansion is as follows:

1) The atoms at the tip and atoms on the opposite edge BCNT were fixed so that they will not return into their initial position after compression. Simulation of the microscope tip operation was achieved by fixing the atoms at the tip of the nanotube. In the modeling process of the interaction of structure surface with a microscope tip, the stretch of the indenter (nanotube) was observed.

2) The optimization of the atomic structure of BCNT by coordinates of all loose atoms was conducted by the empirical method REBO lead to the optimal structure of the system.

3) The shift of the sharp edge at 0.1 Å along the nanotube in 1000fsek was carried out. As result of the simulation, the Van der Waals interaction of the surface of the structure with a microscope tip was found.

Compression/expansion was carried out at a speed of 10 m/sec. It is shown that the destruction of BCNT occurs in the bridge area after 19 psec in tension, and the destruction the hollow nanotubes occurs after 14 ps. Areas of destruction of the atomic structure are shown in Figure 1. Tensile by 5% led to the BCNT destruction and tensile by 3% led to the hollow nanotubes destruction. Therefore one can conclude that the BCNTs are more mechanically resistant compared to the hollow nanotubes.

![Fig. 1. BCNT destroyed in the area of the bridge.](image1)

![Fig. 2. BCNT destroyed in the area of the bridge.](image2)
The tip BCNT become concave in the compression process after 45 psec. The chemical bond lengths reduced from 1.42 Å to 1.38 Å in the bridge and tip areas. The destruction of nanotubes occurred after 51 psec (Fig. 2).

2.3. Emission properties of bamboo-like nanotubes
The study of electronic properties of the infinite BCNT with increasing distance between the bridges requires a series of calculations. The optimization process, i.e. the finding the equilibrium structure by minimizing the total energy, was carried out for the bamboo-like nanotube with a length of 14.58 nm and a diameter of 2.024 nm with three bridges. This structure contains about 4000 atoms. The optimization process using the quantum-chemical method is problematic for such a structure due to the large number of atoms. The use of parallelized computing algorithm requires a large amount of computing resources and time and, therefore, is not rational. Optimization process was carried out by using the AMBER force field of molecular dynamics [13].

Infinite BCNTs were modeled with a translation vector [14]. Four types of cells, having a length of 2.071 nm 2.317 nm 2.564 nm and 2.811 nm, were chosen as the repeating BCNT cells. The distance between the bridges was being increased with elongation of the cell. The obtained ionization potential and the energy gap of bamboo-like nanotubes with different distances between the bridges are shown in Table 1. It was found that the ionization potential and emission properties of infinite bamboo-like nanotubes with the distance between bridges of the 2.811 nm exceed those of the infinite hollow nanotubes. Ionization potential of an infinite hollow nanotube is equal of 6.2 eV. In this regard, further we consider the change of the ionization potential of bamboo-like nanotubes with the distance between the bridges 2.811 nm and with an increase of potassium atoms concentration. The increase of the latter up to five in each unit cell with a length of 2.811 nm leads to a decrease in the value of the ionization potential by 0.2 eV. Consequently, we can assume that the emission properties can be controlled by potassium atoms adding or removal.

| Distance between bridges, nm | Ionization potential, eV | Energy gap, eV |
|-----------------------------|-------------------------|---------------|
| 2.071                       | 6.436                   | 0.593         |
| 2.317                       | 6.349                   | 0.508         |
| 2.564                       | 6.348                   | 0.519         |
| 2.811                       | 6.065                   | 0.019         |

Table 1. Energy parameters of BCNT with different distances between bridges

Fig. 3. Change of the ionization potential depending on the number of potassium atoms in the repeating unit cell

Fig. 4. Change of the energy gap depending on the number of potassium atoms in the repeating unit cell
3. Conclusion

In the paper the properties of the bamboo-like nanotubes were investigated. First of all, it was established that 2.024 nm diameter of the bamboo-like nanotubes is the smallest one for the stable nanotubes (i.e. it is the smallest diameter of all the existing BCNTs).

Also, it was shown that the maximum stress appearing in the atomic framework of the BCNTs of 2.024 nm, equals to 8.77 GPa. It is the stress at which no destruction for the bamboo-like nanotube is observed. On the other hand, under the dynamical stretching with the speed of 10 m/sec all the BCNTs are being destroyed after 19 psec. The stress at which the destruction is observed, equals to 11 GPa. It should be mentioned that under the similar conditions of the loading, the hollow carbon nanotubes are being destroyed after 14 psec, suffering much lower stress.

The BCNT tip deformation was also studied in the work. The change of its atomic framework configuration was observed after 45 psec under the condition of the 10 m/sec speed dynamic loading. Its destruction was found in 51 psec.

Because of all the aforementioned results, and also due to the fact that the BCNTs are ultrathin and heavy-duty nanostructures, one can conclude that they can be used as nanoindenters.

Mathematical model of the infinite bamboo-like carbon nanotubes was developed. Also, the emission properties of the infinite bamboo-like nanotubes with diameter of 2.024 nm and a distance between the bridges 2.811 nm were studied by tight-binding method. It was found that the ionization potential of these nanotubes decreased by 0.1 eV in comparison with the infinite hollow nanotubes. The adsorption of potassium atoms on the surface of an infinity bamboo-like nanotubes was also modeled by tight-binding method. It was revealed that the emission properties of BCNT were improved by inserting the potassium atoms in the atomic structure (with a concentration of 0.59% and above in each repeating cell). In this case, the ionization potential has decreased by 0.35eV. Based on these results, one can conclude that the bamboo-like nanotubes could serve as a more prospective material for the construction of nanoemitters than the hollow nanotubes.

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