Study of modification of carbon univariate nanostructures with boron atoms impurities

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Abstract. The article describes peculiarities of structure and influence on electron-energy properties of carbon nanotubes, whose surface is structurally modified with replacing boron atoms. Various substitution options and the percentage of boron and carbon atoms are considered, the width of the band gap is established depending on the percentage of boron atoms on the surface of the nanotube. The results presented in this article can form the basis for recommendations on the possibility of managing the conductive properties of nanomaterials.

1. Introduction
The latest nanotechnologies, along with information and biotechnology, are the basis for the scientific and technological revolution of the 21st century, comparable and even superior in scale to the progress in technology caused by scientific discoveries of the 20th century. In recent years, nanotechnology has become one of the most significant areas of knowledge. It is one of the most promising branches of high technology and is considered a systemic factor in the economy of the 21st century. In addition to stimulating the development of a new system of methods, technical skills and tools for all production activities based on movement from individual atoms and molecules to the product, nanotechnologies also provide new approaches to solving many social problems.

Nanotubes have been found to exhibit unique sorption and conductive properties due to their structural features, which include the above mentioned high specific surface area, chirality and composition features [1, 2]. Due to the high sensitivity of the nanotubes to even the micro amounts of different substances, expressed in changing the conductive properties of the material, they can be used as various filters and sensors (chemical and biological) [3,4]. The working principle of filters and sensors is based on changing the voltamper characteristics of the nanotube during sorption of molecules of a certain grade on the surface of the tubes. Nanotube sensors have a number of advantages, in particular: high selectivity, rapid response and high recovery rates over conventional ones.

But carbon nanotubes are not the only material with a tubular structure. To date, a number of nanotubes have been obtained, the surface of which consists not only of carbon atoms, but also of other atoms, for example, boron, nitrogen, silicon, etc. For example, boron nanotubes [5-8], regardless of surface geometry and diameter, have semiconductor properties. Due to this stability, it can be expected that boron tubular nanosystems will be in demand as highly efficient semiconductors, nanoelectronics samples and in other fields.

One method of modifying carbon nanotubes is to replace carbon atoms with other elements. Among them the nanotubes, received in 2004 by replacement of atoms of carbon of a surface of CNT
with pine forest atoms in gas flow of BCl$_3$ [9], are especially attractive. Such nanotubes are stable semiconductors and, as studies have shown, exhibit better sorption properties compared to pure carbon [10], which also makes them promising for using in sensor devices.

Therefore, the study of structural features and electron-energy characteristics of boron-containing nanotubes with a different content of boron atoms impurities is important and relevant. This article considers the mechanism for modifying carbon nanotubes with boron atoms in maximum (50%) and minimum (15%) concentrations, which allows maintaining the periodicity of the nanostructure in achiral nanotubes.

2. Results of the study

Structural features and basic energy characteristics of BC nanotubes of type (n, 0) were studied, when in the structure of a carbon nanotube every second carbon atom is replaced by a boron atom. Figure 1 shows a cluster of nanotubes of type (6, 0).

![Figure 1. Extended cell of BC nanotubes (6.0).](image)

Fragments of (n, 0) type single-layer tubes where n = 4, 6, 8, 10, 12 are considered. Clusters containing n six-atomic boron-carbon cycles along the tube perimeter and two or more elementary layers along its axis are selected as geometric models of the studied nanotubes. Calculations were carried out using the DFT method. The bond lengths between adjacent boron and carbon atoms were assumed to be equal 1.4Å for all nanotube clusters considered. The results of calculations of main characteristics of BC (n, 0)-nanotubes are given in Table 1.

A single-electron spectrum of nanotubes was built, which demonstrated that the levels of atomic orbitals are grouped into analogues of the conduction zone and the valence zone. Analysis of the width of the forbidden slit $\Delta E_g$ calculated as the difference in energies of the upper filled and lower vacant orbitals for the BC nanotubes showed that these structures by the nature of conductivity belong to narrow-slot semiconductors, while the width of the forbidden slit does not change with an increase in the diameter of the nanotube. It has been found, that the main contribution to the valence zone is mainly given by s-orbitals of boron atoms and s- and p- orbitals of carbon atoms. 2p-atomic boron and carbon orbitals contribute to the conduction zone. Values of forbidden slot width are given in Table 3.1.1. The charge value on the boron atoms $Q = 0.8$; a negative charge $Q = -0.7$ appeared on the carbon atoms.


Table 1. Main characteristics of boron-containing nanotubes (n, 0). Calculations of $\Delta E_g$ were carried out using the DFT method using functionality B3LYP.

| (n, 0) | $\Delta E_g$, eV (BC) |
|-------|----------------------|
| (4, 0) | 0.02 |
| (6, 0) | 0.09 |
| (8, 0) | 0.02 |
| (10, 0) | 0.02 |
| (12, 0) | 0.02 |

Next, carbon nanotubes were studied, in which only one atom out of six in the carbon hexagon was replaced with boron. These are the so-called BC$_3$ nanotubes. Figure 2 shows a cluster of such a nanotube type (6, 0).

![Figure 2](image)

Figure 2. Expanded elementary cell BC5 nanotubes (6, 0).

Fragments of single-layer tubes (n, 0) of type where n = 4, 6, 8, 10, 12 are considered. The length of the bond between neighboring atoms, when optimizing the geometry of the structures, turned out to be 1.4 Å. The number of (N) atoms in the nanostructure clusters was as follows: for (4, 0) N = 96 atoms, for (6, 0) N = 144 atoms, for (8, 0) N = 160 atoms, for (10, 0) N = 240 atoms, for (12, 0) N = 240 atoms.

The analysis of the energy curves as a result of the executed calculations by the DFT method with functionality of B3LYP of an electronic and power range of BC$_3$ nanotubes allowed to estimate the width of the energy gap for the chosen type of the nanotube. The results are listed in Table 2.

According to the results of research, a comparative table of characteristics of the scanning process of an imaginary surface containing alkali metal atoms was compiled.

Analysis of the data showed that single-layer BC$_3$ nanotubes are narrow-gap semiconductors. Dependence of forbidden zone width on nanotubes is periodic. Graphs of the band gap width versus nanotubes diameter were plotted. (Figure 3).

Table 2. Width of forbidden slot for REC of single-layer BC$_3$ nanotubes (n, n).

| (n, 0) | $\Delta E_g$, eV (BC$_3$) |
|-------|--------------------------|
| (4, 0) | 0.13 |
| (6, 0) | 0.69 |
| (8, 0) | 0.26 |
| (10, 0) | 0.19 |
| (12, 0) | 0.69 |
The dependence of the energy gap width on the diameter for carbon nanotubes with boron atoms impurities obtained from the analysis of the calculated values of the width $\Delta E_g$, showed the following (see Table 3).

**Table 3.** Dependence of band gap width for boron-containing nanotubes and pure carbon nanotubes on diameter.

| Nanotube diameter, Å | $\Delta E_g$, eV (BC$_5$) | $\Delta E_g$, eV (BC) |
|----------------------|---------------------------|-----------------------|
| (4, 0)               | 0.13                      | 0.02                  |
| (6, 0)               | 0.69                      | 0.09                  |
| (8, 0)               | 0.26                      | 0.02                  |
| (10, 0)              | 0.19                      | 0.02                  |
| (12, 0)              | 0.69                      | 0.02                  |

3. Conclusion
The analysis showed that nanotubes of type $(n, n)$ are dielectrics, and boron-containing nanotubes of type $(n, 0)$ are narrow-gap semiconductors. At the same time, if the concentration of boron atoms impurities is less than 25%, the width of the forbidden zone increases. This can be explained by the presence of inhomogeneities in the charge distribution on the surface of the boron-containing nanotube, since boron atoms accumulate positive charges near themselves, while the electron density is concentrated in carbon atoms.

At the same time, when the equilibrium concentration of boron and carbon atoms is reached, the width of the band gap decreases, till practically zero value. Thus, the main conclusion form the analysis of the energy gap variation for carbon nanotubes with boron atoms impurities is the theoretically proven possibility of controlling the conductivity process in the chosen type of nanotubes.

4. References
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