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The effect of substitution atoms on the electronic properties of carbon nanotubes

© S.V. Boroznin, I.V. Zaporotskova, N.P. Boroznina, A.D. Grigiriev, P.A. Zaporotskov, K.Yu. Verevkina

Volgograd State University,
400062 Volgograd, Russia
e-mail: boroznin@volsu.ru

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Despite the large amount of research on the interaction of carbon nanotubes with various materials, boron (B) and nitrogen (N) remain the most suitable substances for carrying out substitution reactions. For a computer experiment to study the dependence of electronic properties on the concentration of replacement atoms, carbon nanotubes with different concentrations of replacement boron or nitrogen atoms were selected, namely: with a content of 50% (every second carbon atom was replaced by a B or N atom); 25%; and nanotubes, in which only one C atom is replaced by an atom B or N in a hexagon. As a result of the conducted research, it was found that there is a dependence of the band gap width on modifying atoms, as well as charge transfer between carbon and substitution atoms. Based on the results of the analysis of carbon nanotubes containing various concentrations of impurity boron atoms, it can be noted that nanotubes of type $(n, 0)$ containing substitution atoms are narrow-slit semiconductors. When modified by boron atoms, a positive charge is concentrated on them, while nitrogen pulls away the electron density in carbon nanotubes.

Keywords: carbon nanotubes, boron-carbon nanotubes, computer modeling, semiconductors, modification of nanostructures.

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Introduction

Carbon-based nanostructures have been one of the most demanded nanotechnology materials for several decades. Due to their unique properties, they are widely used for various industrial, science and technology applications. However, achievement of stable nanostructures with desired properties is one of the key issues. Functionalization of carbon nanotubes (CNT) is one of the simplest property control methods. This implies modification of sp^2 hybridized nanotubes using atomic substitution reactions with similar heteroatoms or functional groups [1–3]. This method makes it possible to control chemical properties of nanotubes and to modify effectively their capabilities and properties, thus, increasing their applicability [1–3]. Li, B, N, S, P, K and other elements were addressed in the literature as doping substances. Krockel et al. in [4] studies in detail possible potassium-doping of CNT and electron energy structure of the obtained nanomaterial. Some works describe possible sulfur-doping and phosphorus-doping of nanotubes [5–7]. Tavakol et al. in [8] reports about possible use of sulfidized CNT to prevent oxidation processes. The researchers also support their investigations by the data of the Krockel computer experiment carried out using the density functional theory, Monte Carlo , etc. [9]. Saadat et al. in [9] studied the interaction of pure carbon and sulfidized nanotubes with methanol, methanethiol, water and dihydrosulfide.

Despite a large scope of studies of interaction between CNT and various materials, boron (B) and nitrogen (N) are still the most suitable substances for substitution reactions, for which there is a set of prerequisites such as oxidation-reduction properties of heteroatoms that ensure smooth incorporation of heteroatoms into the nanotube lattice [10]. When selecting a doping substance, focus shall be also made on the safety and stability of future material with retaining the main spatial properties of the nanoobject.

Substitution of some nanotube atoms with heteroatoms even at small concentrations substituent atoms may ensure a Fermi energy shift during donor-acceptor reactions. Similar methods were taken as the basis of controlled fabrication of *p*-type or *n*−type nanomaterials because the electron properties of nanotubes show strong dependence on substitution atoms [10–12]. This justifies the importance of studies described in the paper.

The objective of this study is to examine electron energy structure of CNT-based heterostructures containing substitution atoms, perform physical and chemical analysis of nanomaterials and forecast possible scope of applications according to theoretical experiments. To achieve the objective of the study, density functional theory was used to understand the options of substituting some carbon atoms in a nanotube with nitrogen and boron with concentrations of 15%, 25% and 50%. A simulation experiment provided electron energy structure data of CNT with substituent atoms suggesting the influence of substituent atoms on the electronic properties of nanoobjects.

1. Density functional theory

DFT (Density Functional Theory) method with B3LYP functional is based on the combination of three components: Lee-Yang-Parr functional for exchange energy, Becke–Lee–Yang–Parr functional for correlation energy and Jilles−Johansen functional for exchange-correlation energy. Such combination ensures a balance between accuracy and computational efficiency. B3LYP has a good accuracy for calculation of bond energies and geometry [13].

Electron density ρ, that depends on the coordinates of all electrons constituting the system, is the central physical quantity of the DFT method. Electron density created by all electrons of a molecule is calculated as follows

$$\rho(r) = \sum_{i=1}^{N} |\phi_i(r)|^2, \tag{1}$$

where ϕ_i is the electron wave functions.

The Kohn−Sham density functional theory expresses the total system energy as the charge density functional:

$$E[n] = \langle \Psi[n] | (\hat{T} + \hat{U} + \hat{V}_{ext}) | \Psi[n] \rangle = T + U + V_{ext}$$
$$= T_S + V_H + V_{ext} + (T - T_S + U - V_H), \tag{2}$$

where T_S is the Kohn−Sham kinetic energy that is expressed through the Kohn−Sham orbitals, V_{ext} is the external potential acting on the interacting system (at least for a molecular electron−nucleus interaction system), U is the Coulomb interaction energy, V_H is the Hartree energy.

DFT methods differ from each other in the EXC(p) form and the presence of various adjustable parameters.

Correlation exchange functional $B3LYP$:

$$E_{XC}^{B3LYP} = (1-\alpha)E_X^{LSDA} + aE_X^{HF}$$
$$+ b\Delta E_X^{B88} + (1-c)E_C^{VWN} + c\Delta E_C^{LYP}. \tag{3}$$

Here E_X^{LSDA} is the exchange energy using the local spin density approximation; E_X^{HF} is the Hartree-Fock exchange energy; ΔE_X^{B88} is the Becke three-parameter functional of the gradient correction method; E_C^{VWN} is the VWN local spin density approximation to the correlation functional; ΔE_C^{LYP} is one of the most popular correlation functionals proposed by Lee, Yang and Parr; a, b and c are the constants chosen from the experimental data for relatively simple chemical compounds: $a = 0.2$, $b = 0.72$, and $c = 0.81$.

2. CNT containing substituent boron atoms

For the computer experiment, boron-carbon nanotubes with various concentrations of impurity boron atoms were examined, i.e. BC type nanotubes with a boron content of 50% (every other carbon atom was replaced with a B atom), BC_3 type boron-carbon nanotubes with a boron content of 25% and BC_5 nanotubes where only one C atom is substituted with a B atom in the hexagon [14,15]. Figure 1 shows the studied nanotubes to illustrate the relative positions of B and C atoms.

„Zigzag“ $(n, 0)$ nanotubes, where $n = 4, 6, 8, 10, 12$, were chosen for the study. The nanotube cluster length included 8 hexagon layers along the principal longitudinal axis and the number of layers on the nanotube periphery was n according to the structural principle of a convolute nanoobject. Density functional theory was used as the main computational method. Error of this method for the chosen basis set (6-31G with$B3LYP$) verified on 300 compounds by comparing with experimental data give a deviation up to 1 kcal/mol [16,17]. Gaussian software package was used for the calculations. Theoretical study determined a main parameter affecting the electronic properties of nanotubes, i.e. the band gap ΔE_g. The band gap values depending on the tube diameters are shown in Table 1.

The computer experiment also provided data that was used to plot single-electron spectra of nanotubes (Figure 2). Spectral analysis established that atomic orbital levels are grouped into zones that are divided into a valence band and conduction band in accordance with the common designation. Energy gaps calculated as a difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and listed in Table 1 allow the CNT with the content of impurity boron atoms of 50% to be assigned to narrow-gap semiconductors independently on the nanotube diameters. Structural study of atomic orbitals has shown that s- and p-orbitals of a C atom and s-orbitals of a B atom constitute a nanotube valence band. $2p$-orbitals of B and C atoms form a conduction band. Introduction of impurity atoms in the nanotube structure gives rise to nonuniform charge distribution: electron density redistribution takes place and positive charges $Q_B = 0.8$

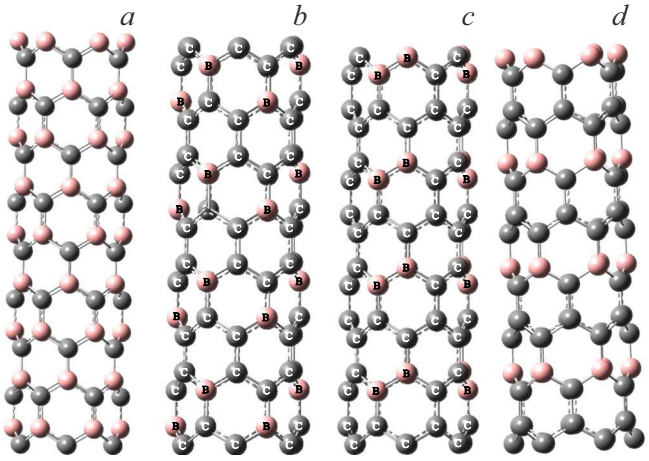

Figure 1. Boron-carbon nanotube clusters with various boron atom concentrations: a — BC nanotube (6,0); b, c — relative positions of boron and carbon atoms in A and B type BC_3 nanotubes; d— atomic ordering option for B and C atoms in the BC_5 nanotube cluster.

Table 1. CNT band gap variation depending on the diameter and content of substituent boron atoms

Nanotube diameter Å	ΔE_g, eV (C)	ΔE_g, eV (BC_5)	ΔE_g, eV (BC_3)		ΔE_g, eV (BC)
			Type *A*	Type *B*	
3.03	0.81	0.13	0.81	0.54	0.02
4.77	0.81	0.69	0.54	0.54	0.09
6.35	0.27	0.26	0.26	0.54	0.02
7.72	0.27	0.19	0.19	0.54	0.02
9.57	0.27	0.69	0.07	0.54	0.02

occur on the boron atoms, and negative charges $Q_C = -0.7$ occur on the carbon atoms.

Then we studied the variation of conductive properties of boron-carbon nanotubes with the decrease in the content of impurity boron atoms. BC_3 nanotubes with the boron content of 25% were the next object of our study. Due to the decrease in the concentration of B atoms, various arrangements of B atoms on the nanotube surface could be considered. Such nanotubes may be called *A* and B type BC_3 tubes (Figure 1, *b, c*) [14,15].

For nanotubes with carbon and boron atom ordering corresponding to type *A* structure, the calculated ΔE_g allowed two important features of the electronic structure to be identified. Firstly, they are semiconductor by the type of conductivity, and secondly, there is a dependence between the diameter and energy gap, i.e.ΔE_g decreases as the diameter increases. Analysis of the electron energy structure of *B* type nanotubes shows that they are assigned to narrow-gap semiconductors. The valence band consists of *s*- and *p* orbitals of C atom and *s* orbitals of *B* atom. The conduction band is formed by the contributions of 2*p*orbitals of both types of atoms. Numerical values of the band gap are shown in Table 1. As for the equilibrium concentration of B and C atoms, introduction of impurity atoms into the nanotube structure gives rise to a non-uniform charge distribution. This causes the occurrence of the positive charge on boron atoms $Q_B = 0.13$ and the negative charge on carbon atoms $Q_C = -0.07$.

Single-electron spectra of the studied CNT types with impurity boron atoms are shown in Figure 2, *b, c*.

Study of the minimum B atom concentration case was the final stage of the study of impurity boron atom influence on the CNT electronic structure. This is the case when only one C atom in the hexagon is substituted with a B atom. Such nanotube may be designated as the BC_5 nanotube. An atomic ordering case for the BC_5 nanotube is shown in Figure 1, *d* for nanotube (6,0).

Analysis of the calculated band gap suggested that BC_5nanotubes by the type of conductivity will be assigned to narrow-gap semiconductors. It was found that, as the nanotube diameter increased, variation of the band gap is periodic in nature. Figure 2, *d* shows single-electron energy spectra (6,0) of BC_5 type nanotubes.

For more convenient evaluation of numerical energy band variation with the increase in diameter for CNT doped with different amount of boron atoms, Table 1 was prepared.

3. CNT containing substituent nitrogen atoms

The feature of heterostructures examined in the computer experiment is the periodic behavior of substituent atom distribution throughout the nanotube surface. To implement this periodic behavior, nitrogen atom concentrations of 50%, 25%, 15% were chosen [13–15]. Relative positions of N and C atoms in the „zigzag“ type nanotube are shown in Figure 3.

As mentioned above, Figure 3 shows a model of CNT clusters with substituted nitrogen atoms that is used for computer experiments. The model consists of four lattice cells. Quantum chemical calculations were performed to get the electronic structure, physical and chemical property data for nanotubes. Table 2 shows the band gap for various diameters of CNT with substituted nitrogen atoms.

Electronic and energy structure data were obtained after construction using the quantum chemical calculations of density of electron states (Figure 4).

Let's consider in more detail individual types of nitrogen-containing CNT. The first study stage included maximum substitution of carbon atoms with nitrogen, i.e. 50%, which corresponds to the CN type nanostructure. For band gap analysis, upper occupied and lower unoccupied molecular orbitals (HOMO and LUMO,respectively) were determined. The difference between them is the band gap. It was found that, as shown in Table 2, this type of nitrogen-carbon nanotubes refers to narrow-gap semiconductor with ΔE_g from 0.4 eV to 0.8 eV. *s*- and *p*-orbitals of carbon atoms and *s*-orbital of nitrogen atoms make the main contribution to the formation of valence band. During formation of conduction bands, energy levels are formed by p-orbitals of carbon and nitrogen atoms. Emerging electron density redistribution between structural elements is another evidence of forming heterostructure. Charge distribution analysis was carried out to support this fact. The analysis established that the electron density is concentrated near the nitrogen atoms ($Q_N = -0.7$) giving rise to a positive charge on the carbon atoms ($Q_C = 0.3$), i.e. CNT modified by substituted nitrogen atoms, due to the emerging charge

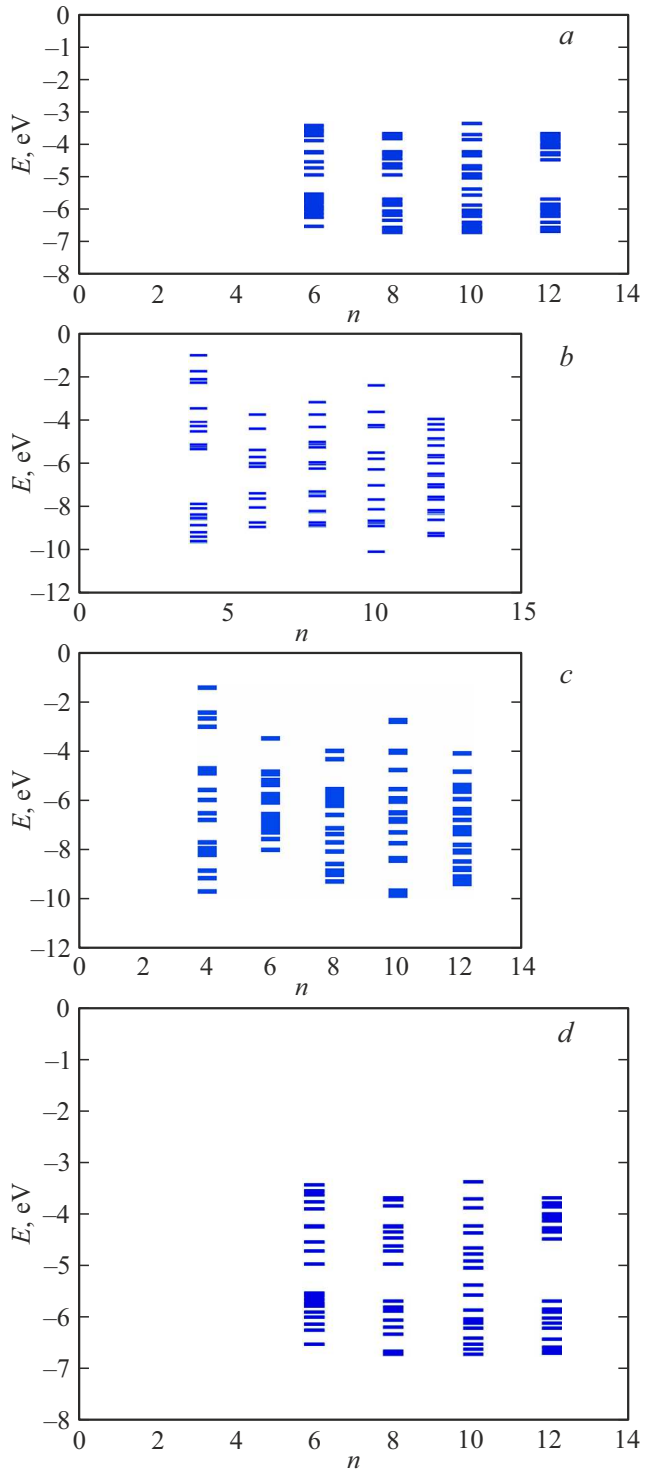

Figure 2. Single-electron energy spectra of a boron-carbon nanotube. Chirality index n is plotted on the X axis in accordance with the common designation used for „zigzag“ nanotubes $(n, 0)$; energy [eV] is plotted on the Y axis: *a* — for the BC structure; *b, c* — for the BC_3 *A* type and *B*type structure; *d* — for the BC_5 structure.

redistribution, may be assigned to heterostructures with controlled band gap and periodic structure.

The next computer experiment stage included the study of CNT with lower content of substituent nitrogen atoms. To ensure periodic behavior, as mentioned above, these were nanostructures with nitrogen percentage of 25% or NC_3 nanotubes. This concentration allows proceeding to two options of relative spatial orientation of C and N atoms that are referred to as types *A* and *B* similar to CNT containing substituted boron atoms [10, 13].

The band gap in them also enables them to be assigned to semiconductors because it is equal 0.5 V. Energy structure analysis showed that the formation of valence band energy levels involved *s*- and *p*-orbitals of N and C atoms, conduction band levels were also formed from *s*- and *p*-orbitals of N and C atoms. Study of the charge redistribution showed that, for this case as well as for the equilibrium concentration, electron density shift towards nitrogen atoms was observed $(Q_N = -0.77)$, and a positive charge $(Q_C = 0.23)$ is in carbon.

Finally, a minimum concentration of nitrogen atoms in CNT was studied. At this concentration, only one carbon atom in the hexagon is substituted with nitrogen. NC_5 type of nanotube structure corresponds to this type of substitution reaction. Figure 3, *c* shows a cluster of this nanotube and atomic ordering in it.

The band gap values obtained through the quantum chemical calculations showed that semiconductor conductivity would correspond to the NC_5 type nanotube, and the energy gap in the nanotubes made it possible to forecast the appearance of half-metallic properties in these nanostructures.

The computer experiments may be used to make the conclusions described below. The „zigzag“ CNT with substituted boron atoms is assigned to narrow-gap semiconductors. For nanotubes, in which the content of substituent boron atoms is lower than 25%, band gap growth takes place. This may be explained by the heterostructure and emerging charge distribution nonuniformity that are caused by the appearance of substituent boron atoms. They are the

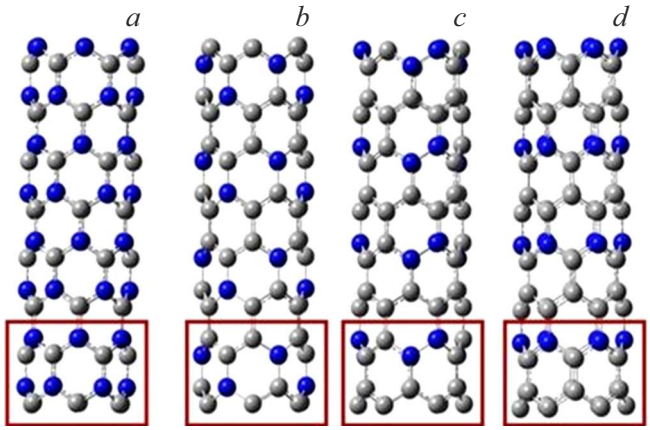

Figure 3. CNT clusters with various nitrogen atom concentrations: *a* — 50%; *b* — 25% type *A*; *c* — 25% type *B*; *d* — 15%.

Table 2. Band gap for CNT with various content of nitrogen atoms

$(n, 0)$	ΔE_g, eV				
	C	NC_5	NC_3 type *A*	NC_3 type *B*	NC
(4,0)	0.81	0.86	0.73	0.43	0.81
(6,0)	0.81	0,59	0.51	0,43	0.51
(8,0)	0.27	0.43	0.62	0,40	0.51
(10,0)	0.27	0,46	0.56	0,46	0.48
(12,0)	0.27	0,43	0.56	0,46	0.46

Note. Values for a pure carbon nanotube are shown for comparison.

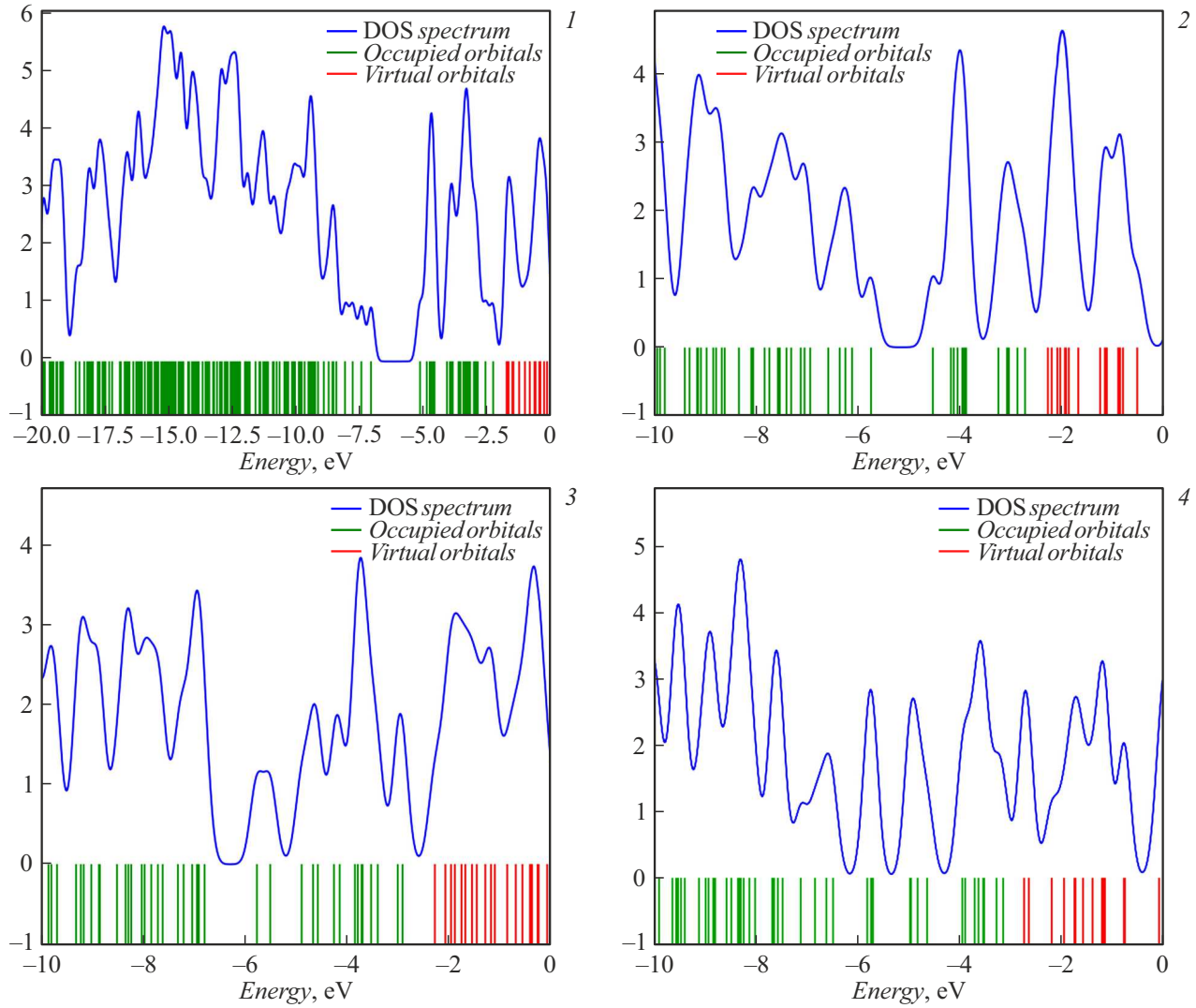

Figure 4. Examples of densities of states for CNT modified by substituent nitrogen atoms: *1* — for the NC structure; *2* — for the NC_5 structure; *3* — for the NC_3 structure type *A*; *4* — for the NC_3 structure type *B*.

centers of positive charges in the nanotube, and the electron density moves towards carbon atoms. With the increase in the concentration of substituent boron atoms to 50%, decrease in the band gap to almost zero values is observed, i.e. introduction of substituent boron atoms allows control of CNT band gap and electronic properties, which was proved by means of the simulation experiments and comparison between the experimental data and real observation data.

The quantum chemical calculation data, in particular, boron atom arrangement and concentration options for CNT, were supported by agreement with the experimental data. Zigzag is the most stable type of boron-containing

nanotubes. This was supported by the quantum chemical calculations using the density functional theory. It was also found that the minimum concentration of impurity boron atoms leading to the uniform boron distribution over the nanotube surface and forming a complete heterostructure with carbon corresponded to 15%, i.e. to the BC_5 structure. It was also found that all CNT containing impurity boron atoms were narrow-gap semiconductors with inverse dependence of the band gap on the nanotube diameter.

The possibility of using CNT containing different concentrations of substituent nitrogen atoms (15, 25, 50%) as nanoelectronic device components was proved theoretically. Band gap variation is observed in carbon nanotubes with the same diameter during the substitution reaction with different nitrogen atom concentrations. The band gap values enable all studied nanotubes to be assigned to narrow-gap semiconductors. Formation of a heterostructure based on CNT with substituted nitrogen atoms may be also suggested because electron density transfer to nitrogen atoms and positive charge localization near carbon are observed in all cases. Study of periodic structures and, in particular, two types of N atom ordering in nanotubes containing 25% of nitrogen made it possible to focus on the considerable contribution of the relative positioning periodicity of nitrogen and carbon atoms in nanotubes to the formation of heterostructures due to emerging charge redistribution. Moreover, grouping and relative positions of nitrogen atoms are essential to control nanotube properties. When studying the type *B*nanotubes where N atoms are grouped in pairs, anomalous behavior of the dependence of band gap on diameter is observed. This is direct dependence of band gap on diameter, though inverse dependence usually takes place. The obtained results are critical for design and engineering of nanoelectronic and microsystem components and assemblies. This is associated with the fact that the data obtained from the theoretical study proves that the refractive index and conductivity of a medium may be controlled due to implementing the reaction of carbon substitution for nitrogen in various concentrations.

Conclusions

The computer experiments carried out to study the dependence of electronic properties of CNT on substituent atoms established the following. Substituent atoms affect the electronic properties by changing the band gap through the appearance of impurity energy levels. Due to the electron density redistribution, the studied nanomaterials may be assigned to heterostructures, however, the electron density shifts to carbon atoms during substitution with boron atoms, and, vice versa, electron density shifts to substituent atoms during substitution for nitrogen.

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Conflict of interest

The authors declare no conflict of interest.

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