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Research Article

# Nitrogen-carbon nanotubes as a basis for a new type of semiconductor materials for electronics devices

Irina V. Zaporotskova[1], Sergey V. Boroznin[1], Natalia P. Boroznina[1], Evgeniy S. Dryuchkov[1], Kseniya Yu. Verevkina[1], Yulia V. Butenko[1], Pavel A. Zaporotskov[1], Lev V. Kozhitov[2], Alena V. Popkova[3], Aleksandr D. Grigoriev[1]

*1 Volgograd State University, 100 Universitetsky Ave., Volgograd 400062, Russian Federation*

*2 National University of Science and Technology "MISIS", 4-1 Leninsky Ave., Moscow 119049, Russian Federation*

*3 JSC "Research Institute NPO "LUCH", 24 Zheleznodorozhnaya Str., Podolsk 142103, Russian Federation*

Corresponding author: Irina V. Zaporotskova (zaporotskova@volsu.ru)

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## Abstract

The use of semiconductor nanomaterials is currently considered to be one of the most promising device optimization methods since those materials allow controlling the electronic properties and possess high mechanical and thermal strength, providing for long device service life without the necessity of replacement or seeking new solutions. The parameters of the electronic and energy structure of new semiconductor nanomaterials based on carbon nanotubes containing substitution atoms have been studied. The test carbon nanotubes contained specific substitution atom concentrations (15, 25 and 50%). A relationship has been drawn between the band gap, conductivity and optical properties of the materials. Data on the band gap and conductivity as functions of substituting nitrogen atom concentration and tube diameter have been reported. The experimental band gap data suggest that the nanotubes in question are narrow-gap semiconductors. One can also conclude that a new semiconductor material has been synthesized on the basis of carbon nanotubes with substitution nitrogen atoms since the test tubes exhibit a redistribution of electron density towards the nitrogen atoms and positive charge localization in the vicinity of the carbon atoms. The results are of utmost importance for the design and fabrication of components and units for nanoelectronics and microsystems: our theoretical study has confirmed the possibility to control the refraction index and conductivity of media by implementing a carbon-for-nitrogen substitution reaction to various concentrations. Thus, a new electronics material has been studied, i.e., carbon nanotubes modified by substitution of nitrogen atoms.

## Keywords

carbon nanotubes, nitrogen-carbon nanotubes, structural modification, conductive properties, adsorption, production of nanotubes

## 1. Introduction

Sustained development of human society is impossible without the search for new materials. Current power industry and electronics materials cause environmental pollution, potentially leading to an environmental disaster in the future. Therefore, transition to new materials and their miniaturization is expected to avoid negative impacts [1–4].

The use of semiconductor nanomaterials is currently considered to be one of the most promising device optimization methods since those materials allow controlling the electronic properties and possess high mechanical and thermal strength, providing for long device service life without the necessity of replacement or seeking new solutions. The crystal periodicity and its effect on the refraction index are the most important performance factors if nanostructures with semiconducting properties are used as photonic crystals [5, 6]. The importance of this work follows from the above-listed facts, and the work implies a thorough study of the electronic and energy structure of new semiconducting materials based on carbon nanotubes containing substitution atoms.

The substitution of part of nanotube atoms by heteroatoms can shift the Fermi level even at low impurity concentrations due to donor-acceptor reactions. Similar methods are used for the controlled synthesis of *p* and *n* conductivity nanomaterials since the electronic properties of nanotubes are strongly dependent on the type of the substitution atoms [6–8]. The possibility to control the conducting properties of the materials is important for electronic delay device applications and radiation field control by external modulation. The above possibility is provided from the fact that one can control light parameters in variable conductivity nanostructures, e.g. amplitude, phase and propagation direction, by varying the dielectric permeability of the media as shown in equations below.

The reaction of partial carbon substitution for nitrogen is an efficient tool for controlling the physicochemical properties of carbon nanotubes [9]. Some specific features favoring the substitution are as follows:

– conservation of the shape, curvature and topology of the nanotubes due to the similarity of atomic sizes of the host nanotube material (carbon) and the substituting material (nitrogen);

– potential applications of substituted nanotubes as semiconductor nanostructures are provided by the different electrical negativities of the host and substituting atoms;

– carbon nanotubes with nitrogen-substituted carbon atoms were successfully synthesized and described in a number of reports [10–13].

## 2. Theoretical background of the method

There is a relationship between the band gap and the refraction index of a material and therefore the refraction index can be used for band gap measurement. The refraction index vs band gap dependence has the following form:

$$n_2 = \mathrm{Re}\varepsilon + k^2, \tag{1}$$

where $n$ is the refraction index, ε is the dielectric permeability and $k$ is the imaginary part of the complex refraction index that describes absorption. The relationship between the conductivity σ and the absorption index α can be written as follows:

$$\alpha = \sigma/cn\varepsilon_0, \tag{2}$$

where $c$ is the speed of light and $\varepsilon_0$ is the dielectric permeability of vacuum. There is also a relationship between the band gap and the conductivity:

$$\sigma \sim \exp(-\Delta E_g/2k_B T), \tag{3}$$

where $\Delta E_g$ is the band gap, $k_B$ is Boltzmann's constant and $T$ is the temperature [14]. Thus, a substitution reaction for nanotube modification allows controlling the refraction index of the new type of semiconductor materials.

The semiconductor nanostructures suggested in this work are of great importance for different optical and electronics applications, and therefore the relationship the substitution reaction and the band gap of the materials requires a thorough study. In order to construct a unified system of data on the band gap behavior, we studied semiconductor nanomaterials with different concentrations and ordering of nitrogen atoms. Quantum-chemical calculations of nitrogen-substituted carbon nanotubes were carried out using the density functional theory [15, 16].

## 3. Description of model experiment

A specific feature of the heterostructures studied within the model experiment was a periodic distribution of the substituting atoms over the nanotube surface. This result was achieved by choosing structures containing 15, 25 an 50% nitrogen atoms relative to the total number of atoms in a nanotube cluster, i.e., the so-called $NC_5$, $NC_3$, NC structures, respectively [6, 17, 18]. The mutual arrangement of the nitrogen and carbon atoms in a zigzag nanotube is shown in Fig. 1. Figure 1*a* shows an equilibrium CN structure in which the carbon and nitrogen atoms are arranged in an interchanging manner. Figures 1 (*b* and *c*) show a $CN_3$ structure which allows different mutual arrangements of the nitrogen and carbon atoms in the nanotube. For definitiveness of terms, by analogy with boron-carbon nanotubes [6], the above structures were denoted as A and B type ones as are shown in Fig. 1. Figure 1*d* shows the structure with the smallest number of nitrogen atoms at which a periodic structure forms in a nanotube, i.e., the so-called $CN_5$ nanotube.

As noted above, Fig. 1 shows the nitrogen-substituted carbon nanotube cluster model used for computer simulation experiments. The model consists of four unit cells. Quantum-chemical calculations provided data on the electronic structure of the nanotubes and

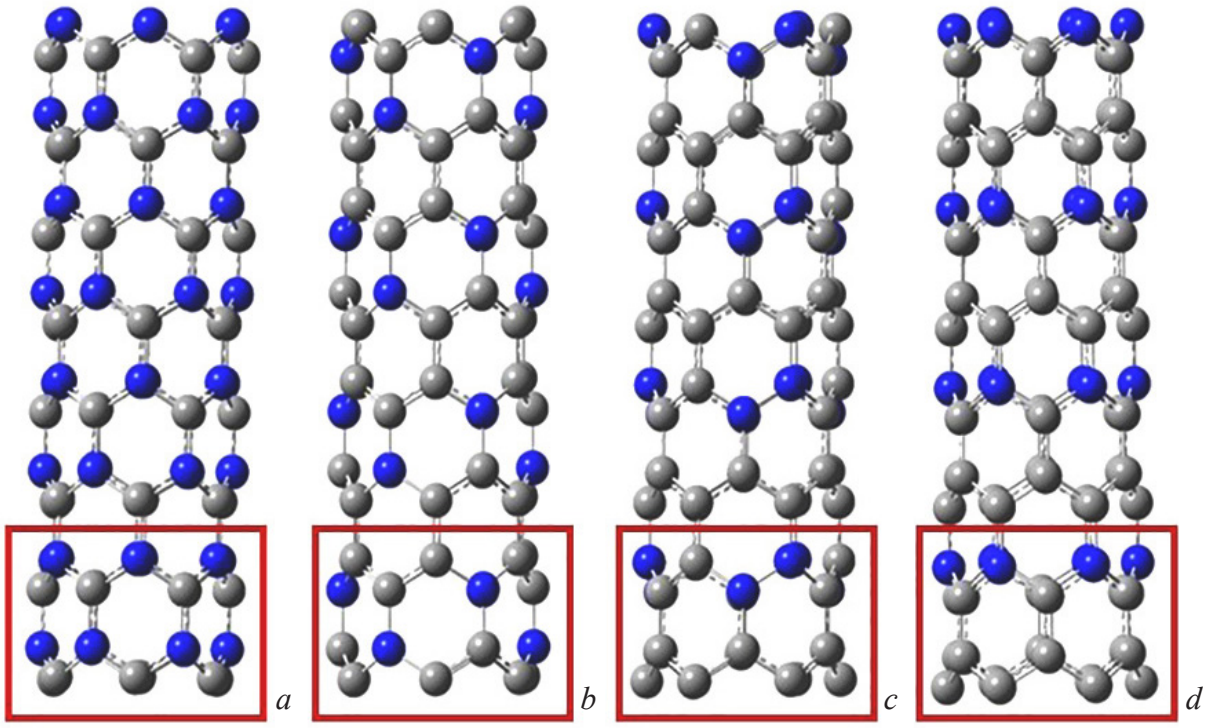


**Figure 1.** Carbon nanotube clusters with different nitrogen atom concentrations: (*a*) 50%; (*b*) 25% type A; (*c*) 25% type B; (*d*) 15%

their physicochemical properties. This work deals with zigzag nanotubes corresponding to chirality ($n$, 0). Nanotube diameter was denoted using different chirality indices. For simulating a periodical structure, we chose different diameter nanotubes with respective chirality indices, i.e., $n$ = 4, 6, 8, 10, 12. The main calculation method was the density functional theory which has already been successfully tested for the solution of similar tasks. According to experimental data [19, 20], for the B3LYP functional and the 6–31G basis set the accuracy of the method is 1 kcal/mole. This result was confirmed by comparing quantum-chemical calculation data with experimental results. After nanostructure optimization the nitrogen-carbon bond length in the nanotube was 0.14 nm. The band gap was calculated on the basis of simulation aimed at checking the possibility to control the optical and conducting properties of the nanostructures. Table 1 summarizes the band gap for nitrogen-substituted carbon nanotubes with different diameters.

**Table 1.** Band gap for carbon nanotubes with different nitrogen atom contents

| ($n$, 0) | $\Delta E_g$ (eV) | | | | |
|---|---|---|---|---|---|
| | C* | $NC_5$ | $NC_3$ | | NC |
| | | | view A | view B | |
| (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 |

* Data for a pure carbon nanotube are presented.

Data on the electronic and energy structure were obtained from electron density of states obtained as a result of quantum-chemical calculations (Fig. 2). In accordance with the fundamentals of solid state physics, during the formation of an electronic structure discrete energy levels form bands conventionally referred to as the valence and conduction bands.

We will now dwell in a greater detail upon some types of nitrogen-containing carbon nanotubes. At the first stage of the study we maximally substituted carbon atoms for nitrogen, i.e., to 50%, which corresponds to a CN type nanostructure. The band gap was calculated from the energies of the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). The difference between these values is the band gap. The results suggest (Table 1) that the nitrogen-carbon nanotubes in question are narrow-gap semiconductors with $\Delta E_g$ of 0.4 to 0.8 eV. The valence band is mainly formed by the *s*- and *p*-orbitals of the carbon atoms and the *s*-orbilats of the nitrogen atoms. The conduction band is formed by the *p*-orbitals of the carbon and nitrogen atoms. Another indication of heterostructure formation is the redistribution of the electron density between the structural components. Charge distribution was studied in order to confirm the above hypothesis. The results showed that the electron density is concentrated in the vicinity of the nitrogen atoms (charge $Q_N = -0.7$), resulting in the concentration of positive charge at the carbon atoms ($Q_C = 0.3$). Thus, the carbon nantoubes modified

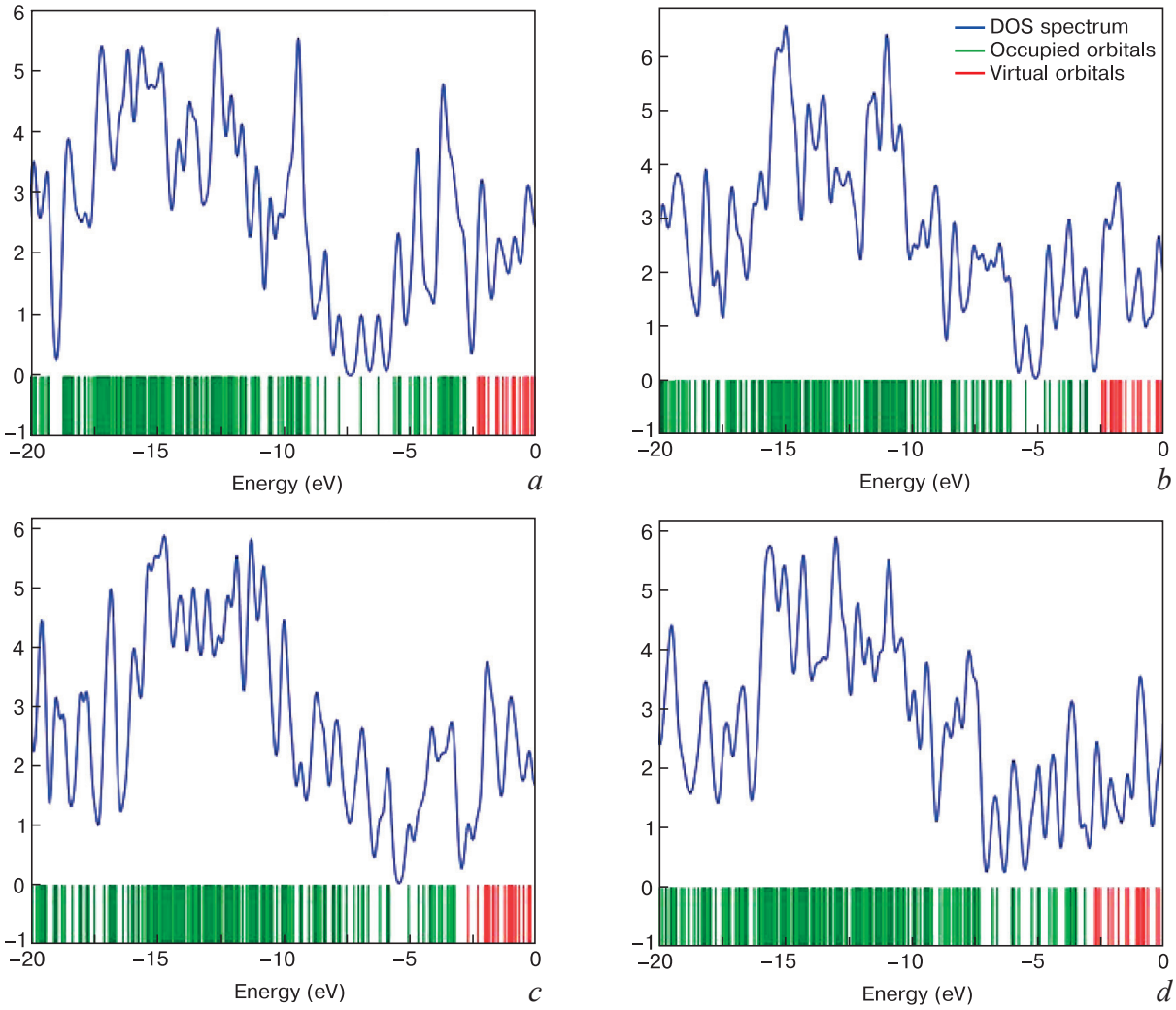


**Figure 2.** Examples of densities of states for carbon nanotubes modified with substitutive nitrogen atoms: (*a*) for NC structure; (*b*) for $NC_5$ structure; (*c*) for $NC_3$ type A structure; (*d*) for $NC_3$ type B structure

by substitution of nitrogen atoms undergo charge redistribution and hence can be considered as a new type of semiconductors with a controlled band gap and a periodical structure.

The next stage of the model experiments was a study of the carbon nanotubes with lower substitution nitrogen atom concentration. As noted above, in order to provide periodicity the nanostructures with a nitrogen concentration of 25%, i.e., $NC_3$ nanotubes, were synthesized [6, 21].

The band gap of the latter nanotubes was also indicative of their semiconducting properties (0.5 eV). Analysis of the energy structure showed that valence band levels are formed by the *s*- and *p*-orbitals of the N and C atoms and the conduction band levels are also formed by the *s*- and *p*-orbitals of the N and C atoms. Study of the

**Table 2.** Conductivity of carbon nanotubes with different nitrogen atom contents

| (*n*, 0) | ε | | | |
|---|---|---|---|---|
| | $NC_5$ | $NC_3$ | | NC |
| | | view A | view B | |
| (4, 0) | $1.4 \cdot 10^{-16}$ | $3.44 \cdot 10^{-14}$ | $1.12 \cdot 10^{-8}$ | $1.14 \cdot 10^{-15}$ |
| (6, 0) | $1.38 \cdot 10^{-11}$ | $4.16 \cdot 10^{-10}$ | $1.12 \cdot 10^{-8}$ | $4.16 \cdot 10^{-10}$ |
| (8, 0) | $1.12 \cdot 10^{-8}$ | $3.78 \cdot 10^{-12}$ | $4.57 \cdot 10^{-8}$ | $4.16 \cdot 10^{-10}$ |
| (10, 0) | $3.39 \cdot 10^{-9}$ | $4.61 \cdot 10^{-11}$ | $3.39 \cdot 10^{-9}$ | $1.52 \cdot 10^{-9}$ |
| (12, 0) | $1.12 \cdot 10^{-8}$ | $4.61 \cdot 10^{-11}$ | $3.39 \cdot 10^{-9}$ | $3.39 \cdot 10^{-9}$ |

charge redistribution showed that, by analogy with the case of equilibrium concentration, the electron density is shifted towards the nitrogen atoms ($Q_N = –0.77$) and a positive charge is formed near carbon ($Q_C = 0.23$).

At the final stage of the experiments we studied the nanotubes containing the lowest concentration of nitrogen atoms (15%). In that case, only one carbon atom per hexagon is substituted for nitrogen. This type of substitution reaction corresponds to the $NC_5$ type nanotubes. Figure 1*d* shows a cluster of the latter nanotube and atomic ordering in it.

The band gap data obtained as a result of quantum-chemical calculations showed that the $NC_5$ type nanotubes have semiconducting properties, the energy gap suggesting potential formation of semi-metallic properties.

Tables 1 and 2 summarize data on the conductivity, band gap and substituting nitrogen atom concentration in order to confirm a relationship between those parameters. Table 1 contains data on the band gap as a function of substituting impurity diameter and concentration, and Table 2 shows data on the conductivity as a function of the above parameters.

## 4. Conclusion

The possibility of using carbon nanotubes with different substituting nitrogen concentrations (15, 25 and 50% of total number of atoms) as nanoelectronic device components was theoretically proven by studying the electronic and energy structure of the nanotubes using the quantum-chemical calculation method of the density functional theory. The band gap of carbon nanotubes having the same diameter changes as a result of a substitution for nitrogen atoms in different concentrations. The band gap data for the nanotubes suggest that the test nanotubes are narrow-gap semiconductors. Another conclusion is the formation of a new type of semiconductor nanomaterials, i.e., nitrogen-substituted carbon nanotubes because all the test nanotubes exhibit a transfer of the electron density towards the nitrogen atoms and positive charge localization near carbon. Studies of the periodic structures, e.g. two types of nitrogen atom ordering in the nanotubes containing 25% nitrogen, showed a significant contribution of a periodic mutual arrangement of the nitrogen and carbon atoms in the nanotubes to the formation of semiconductor nanostructures due to charge redistribution. The configuration and mutual arrangement of the nitrogen atoms are important for controlling the nanotube properties. B-type nanotubes in which the nitrogen atoms are arranged in pairs exhibit an anomalous dependence of the band gap on nanotube diameter. In the test nanotubes the band gap depended linearly on nanotube diameter although typically it exhibits an inverse dependence. The results of this work are of utmost importance for the design and fabrication of components and units for nanoelectronics and microsystems: our theoretical study confirmed the possibility to control the refraction index and conductivity of media by implementing a carbon-for-nitrogen substitution reaction to various concentrations. Thus, a new electronics material has been studied, i.e., carbon nanotubes modified by substitution of nitrogen atoms.

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