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Doped Carbon Nanotube Properties

Viktor Griadun
Zaporizhzhia National Technical University
Ukraine

1. Introduction

The last twelve years have seen enormous growth in many aspects of doped carbon nanotubes. The idea of doping carbon nanotubes has come from microelectronics and now develops both in a traditional donor-acceptor direction (Miyamoto et al., 1995; Lee et al., 1997; Rao et al., 1997; Grigorian et al., 1998; Esfarjani et al., 1999) and in a number of new aspects of application. Among recent trends of application of a doping of nanotubes it is necessary to term such as forming for them magnetic properties (Esfarjani et al., 2003; Farajian et al., 2002), change of their optical performances (Bondarev, 2007), embodying of hydrogen storages (Zidan et al., 2003), amplification of catalytic properties (Gong et al., 2009) and improving of emission characteristics (Yao et al., 2002).

In the present chapter we discuss influence of impurities on properties of semiconductor carbon nanotubes with chiral vectors (10,0) and (6,5) which are representative of groups of nanotubes of type "zigzag" and the twirled chirality, accordingly.

At doping nanotubes usually view an intercalation of impurity inside of a nanotube or in space between separate nanotubes. We view doping nanotubes in traditional sense when impurity ranks one of atoms of a nanotube. It allows to hope, that impurity after such localization will not be lightly to migrate in a nanotube or between separate nanotubes. At such approach to a problem of doping of a periodic nanostructure presence in it of vacancies is supposed. Energy of forming of vacancy in a nanotube makes 5...7 eV (Griadun, 2006). It is a little bit more in comparison with energy of forming of vacancy in silicon, but nevertheless leaves probability of substantial existence of vacancies in nanotubes.

Profound knowledges are necessary for an effective utilization carbon nanotubes in nanoelectronic about their local electro-physical performances. In particular extensive data on concentration and parameters of the impurity centers by means of which it is possible to shape fields with the given type and the quantity of an electrical conductivity reproduced by quantities of a lifetime and a diffusion length of non-equilibrium charge carriers are necessary.

Interest to these examinations is called by necessity of development of designs of integrated transistors and logical units for build-up of complete sets of integrated circuits with use semiconductor carbon nanotubes (Martel et al., 1998; Derycke et al., XXXX).

The solution of a problem guesses an opportunity to drive equilibrium concentrations of electrons and holes in semiconductor carbon nanotubes by their doping.

2. Doped carbon nanotube with indices (10,0)

2.1 Method of modeling and base model of the (10,0) carbon nanotube

Models developed within the limits of a method of molecular mechanics model operation MM + (Berkert & Allinger, 1982) with next parameters:

a quadratic and a cubic stretch term in the potential;

atom types;

nonbonded electrostatic interactions are calculated using bond dipole, which values come from the MM+ stretch parameters;

the electrostatic contribution comes from defining a set of bond dipole moments associated with polar bonds;

cutoffs determine the distance limits for calculating nonbonded interactions of the periodic nanostructure;

inner cutoff radius is the maximum interatomic distance for full nonbonded interactions - 10 Å;

outer radius is the minimum distance at which nonbonded interactions are set to zero - 14 Å.

The base model of the nanotube consisting from two hundred of atoms of carbon, is presented on Fig. 1. In models aromatic bonds, providing interacting of valence electrons of carbon atoms are used.

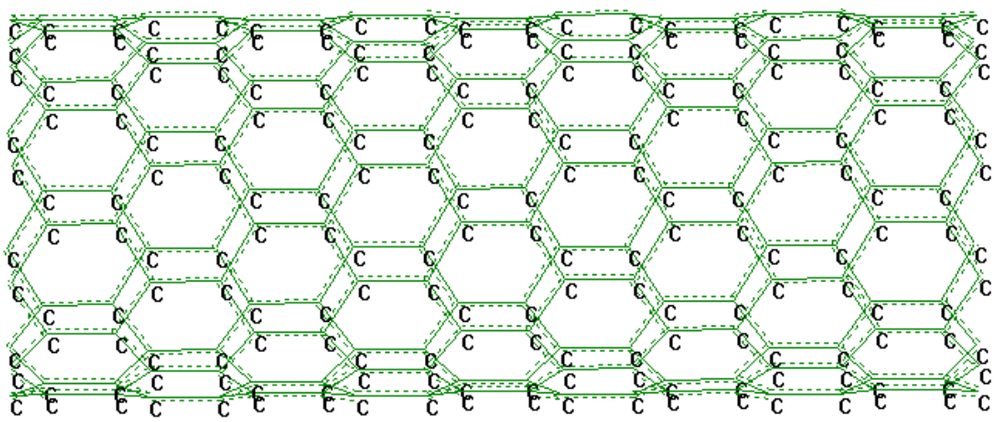

Fig. 1. Basic model of the carbon nanotube with indices (10,0).

The energy-band structure of a nanotube was calculated by the Extended Hückel method (Hoffmann, 1963). The total energy of 200-atomic model of a nanotube has made quantity -323079.99 kcal/mol. On the diagram of its energy structure of a forbidden gap (Fig. 2) is observed a series of levels with energies: -10.60226; -10.37579; -10.37578; -10.36441; -10.36440; -10.30684; -10.27539; -10.26634; -10.26634; -10.24621; -10.24621; -10.19875; -10.19875; -9.6362; -9.6362 eV - matching orbitals with numbers 401 - 415, accordingly.

All from the termed orbitals to a greater or lesser extent match to edges of a nanotube, for example orbital 413 (Fig. 3), and higher orbitals match to a volume part of a nanotube.

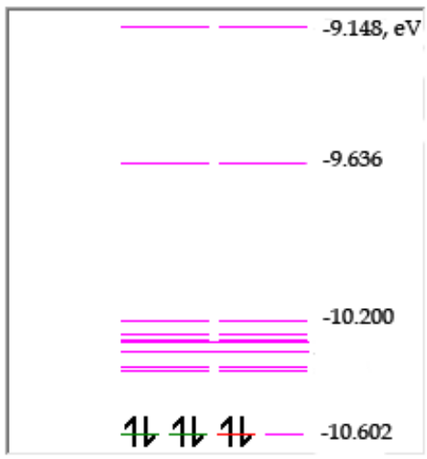

Fig. 2. Structure of a forbidden gap of the nanotube with indices (10,0).

Thus, in a forbidden gap of a nanotube is 30 electronic states matching 15 orbitals. A part from viewed states match to the dangling bonds on edges of a nanotube. For acknowledging this we shall simulate passivation of dangling bonds by atoms of hydrogen.

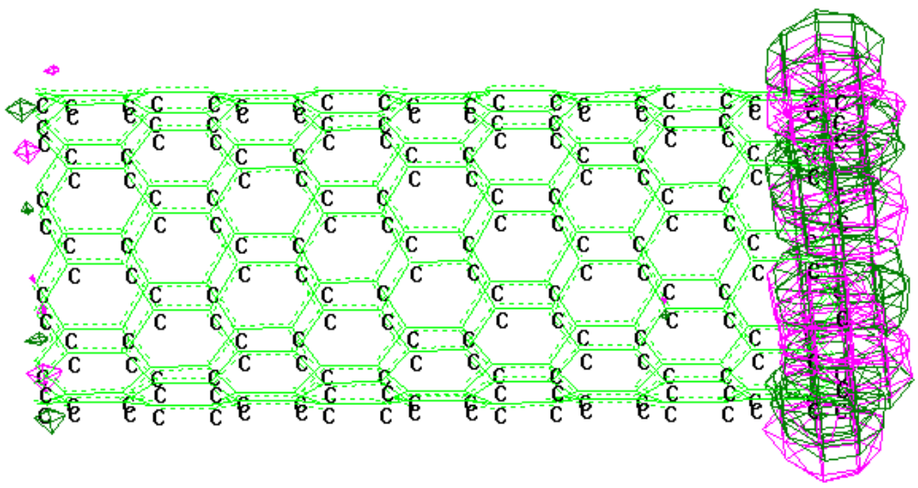

Fig. 3. Orbital 413 of the carbon nanotube with indices (10,0).

On Fig. 4 the model of a 200-atomic nanotube after hydrogen endings and geometrical optimization of nanostructure within the limits of a method of molecular mechanic modeling MM + is figured. Apparently on the model, atoms of hydrogen have filled 20 dangling carbon bonds - on 10 on each edges of a nanotube. Thus, the remained three orbitals feature six states which parent of origination is unknown.
The band of energy diagram in the field of a forbidden gap (Fig. 5) after passivation by hydrogen of the broken off bonds of a nanotube on its edges essentially differs from the diagram of the starting model figured on Fig. 2:

1) The forbidden gap has essentially cleared from energy levels - from 15 remains only 5, that is 10 orbitals that matches to 20 electronic states, were moved in a valence band;
2) Three from five remained energy levels in a forbidden gap should be the acceptor as they are close to a valence band with energies -10.44002 eV (an orbital 411), -10.41608 eV (an orbital 412), and -10.41608 eV (an orbital 413);
3) Passivation by atoms of hydrogen has affected quantity of energy of a ceiling of a valence band (an orbital 410) which has made -10.44002 eV (before passivation was -10.60226 eV);
4) The magnification of energy in item 3 is caused by electronic states of atoms of hydrogen;
5) Passivation by atoms of hydrogen has affected quantity of energy of a bottom of conduction band (an orbital 416) which has made -9.156353 eV (before passivation was -9.147926 eV);
6) The breadth of a forbidden gap of viewed model has made quantity 1.2837 eV (before passivation was 1.4543 eV);
7) The overestimated value of an energy gap in this case is caused by a trace amount of atoms and, accordingly, small length of a nanotube 19.6 Å.

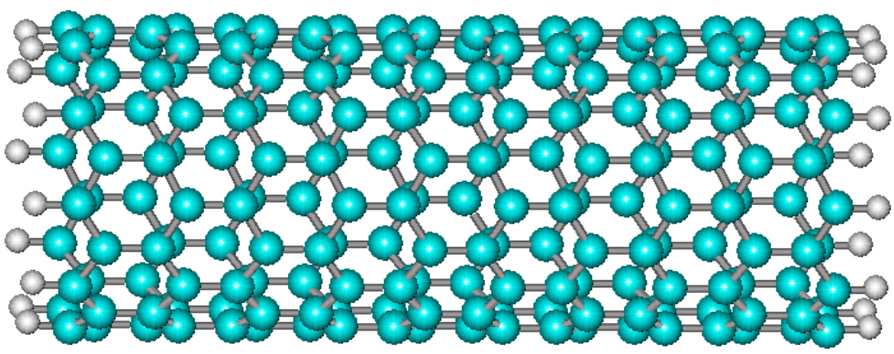

Fig. 4. Hydrogen endings of the carbon nanotube with indices (10,0).

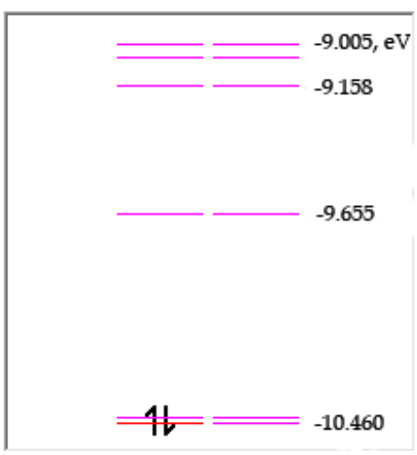

Fig. 5. Structure of a forbidden gap of the (10,0) nanotube after hydrogen endings.

Analogous calculations are lead also for the nanotubes consisting from three hundred and four hundred of atoms of carbon in length ~ 30.15 and 40.63 Å, accordingly. Hydrogen endings of this models also well refines forbidden regions of the energy levels matching broken off bonds. The breadth of a forbidden gap has naturally decreased up to values 1.06 and 0.90 eV, accordingly for 300-atomic and 400-atomic models of nanotubes.

2.2 Doping carbon (10,0) nanotube by atom of boron

Simulation of doping of the nanotube by atom of boron we shall carry out within the limits of a method of MM +, exchanging in the program of basic model the chosen atom of carbon on atom of boron (Griadun, 2007). Thus we can use aromatic bonds of atom of boron with atoms of carbon or exchange them on single bonds, as boron trivalent. We shall consider also at model operation spin multiplicity of a nanostructure.

The geometry of a 200-atomic nanotube doped by atom of boron, is presented on Fig. 6. We see, that at modeling of impurity of boron by aromatic bonds with atoms of carbon the nanostructure distorts feebly. In case of single bonds B-C the nanostructure noticeably distorts in the field of localization of atom of boron. It is related by that single bonds B-C are longer than aromatic on 0.08 Å.

Extended-Hückel energy of the nanostructure with aromatic bonds of atom of boron is less than energy of the nanostructure with single bonds on 2.22 kcal/mol, therefore it is necessary to expect, that in real experiment embodying of the nanostructure with aromatic bonds of atom of boron is more probable.

The energy band diagram of the viewed nanotube doped by atom of boron (Fig. 7a), differs from an energy-band structure of basic model (Fig. 2), however, only quantities of values of energy levels. The expected new acceptor level localized on atom of boron, we do not observe. As well as in basic model three acceptor energy levels, but with other values of energy are observed: -10.60; -10.38 and -10.37 eV. It, visible, is related by that bonds B-C the 1S-electron of atom of boron shares. Except for that removal of degeneration of some orbitals is observed, for example orbitals 414 and 415 with energy -9.636 eV borrow levels with energies -9.641 and -9.611 eV.

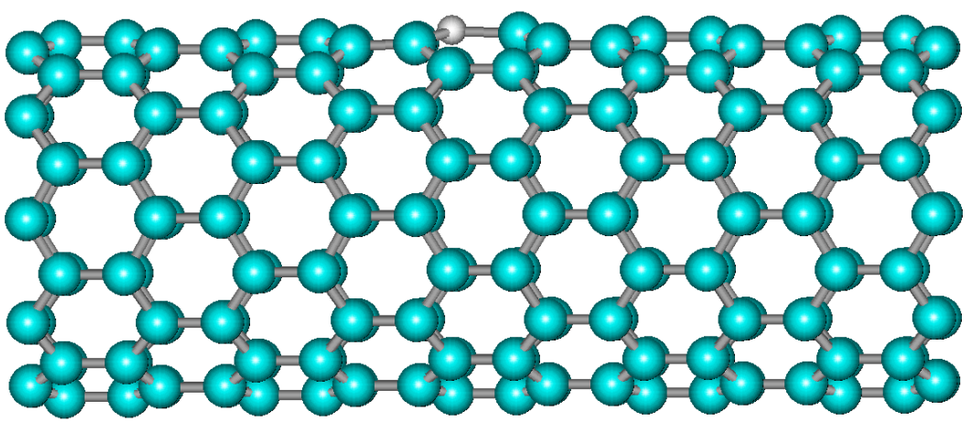

Fig. 6. Geometry optimised model of the carbon B-doped (10,0) nanotube with aromatic bonds B-C.

Hydrogen endings of a nanotube doped by atom of boron practically does not influence geometry of a nanostructure near to atom of boron, however noticeably influences its energy distribution (Fig. 7b). Really, upper occupied level HOMO-0, featured 410-th orbital, has energy -10,46021 eV. Following three orbitals with numbers 411 - 413 are at levels -10.45723, -10.43564, and -10.42292 eV, accordingly. As a whole, such effect is normal as levels of energy of electrons of hydrogen atoms have placed in a valence band and biased its ceiling on 0.15 eV upwards.

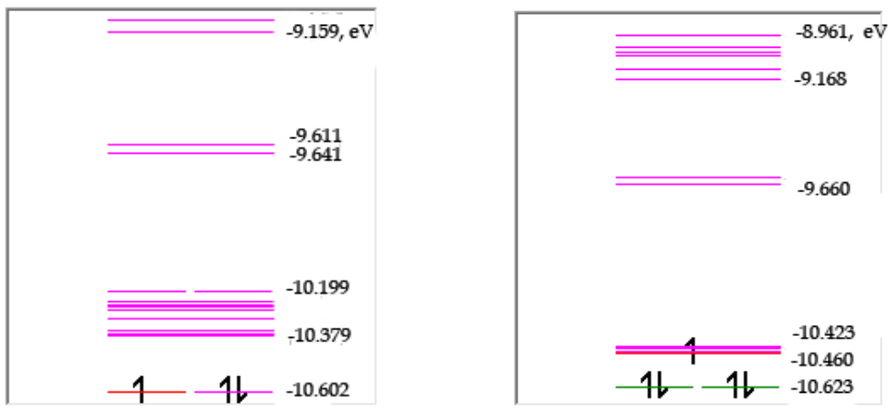

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Fig. 7. Energy band structure of the B-doped (10,0) carbon nanotube before (a) and after (b) hydrogen endings.

2.3 Doping of a carbon (10,0) nanotube by atom of nitrogen

The atom of nitrogen also is well inscribed in geometry of a nanotube, not calling essential strain of its nanostructure (Fig. 8). It is caused by that lengths of bonds N-C and C-C differ a little - 1.28 Å and 1.40 Å, accordingly.

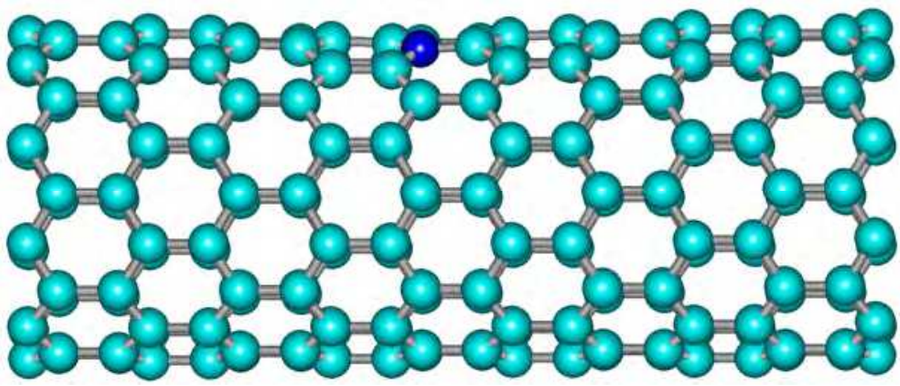

Fig. 8. Model of the nanotube with indices (10,0) doped by atom of nitrogen.

The energy band distribution of a nanotube without hydrogen endings, doped by atom of nitrogen, is presented on Fig. 9a. Under effect of impurity atom in a spectrum of energy levels of a nanostructure there was an orbital filled by an electron the number 401. This

orbital matches to the fifth valence electron of atom of nitrogen and is presented by an energy level equal to quantity -10.6018 eV. The ceiling of a valence band of a model nanostructure is featured by an orbital the number 400 with energy -10.6023 eV. Thus, the extrinsic energy level of atom of nitrogen will not display the donor properties as is near to a valence band, it only will neutralize the inferior acceptor level of a basic nanotube.
In case of nitrogen doping a carbon nanotube with hydrogen endings, the fifth valence electron of atom of nitrogen also occupies the inferior acceptor level near to a valence band (Fig. 9b). Quantity of energy of a level which value makes in this case -10.4579 eV varies only.

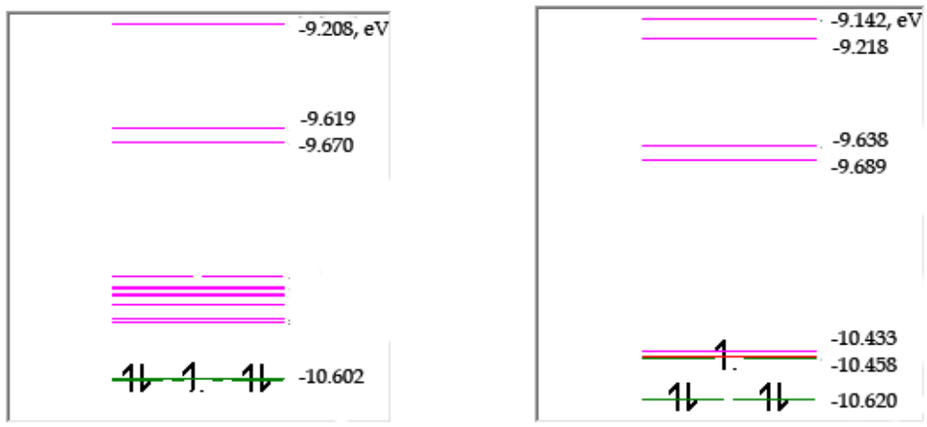

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Fig. 9. Effect of impurity atom of nitrogen on energy spectrum of the carbon (10,0) nanotube before (a) and after (b) hydrogen ending.

Thus, doping by atom of nitrogen of a carbon nanotube with indices (10,0) does not result in to formation of a donor centre, and only results in to blocking of one of acceptor levels of a nanostructure.

2.4 Doping of a carbon (10,0) nanotube by atom of aluminium

Atom of aluminium as the device of the third group, well approaches for doping carbon nanotubes. As if to its influence on geometrical and other properties of a carbon nanotube with coefficients (10,0) we shall view on model of a nanostructure in which atom №133 of the basic model of nanotube we shall replace with atom of aluminium. After geometrical optimization of a nanostructure in which aromatic bonds Al-C use, the model gets a view figured on Fig. 10.
We see, that the atom of aluminium is not inscribed in wall of a nanotube, but located in immediate proximity from it apart 1 Å. Besides atoms of carbon with which bound atom of aluminium, are noticeably drifted for limits of a nanotube. In case of use in model of a nanostructure of single bonds Al-C results in to even greater infringements of geometry of a nanotube. The atom of aluminium settles down thus apart 1.2 Å from geometrical wall of a nanotube. The Extended Hückel calculation of energy distribution in area of a forbidden gap of the Al-doped nanotube is presented on Fig. 11.

Fig. 10. Optimised geometry of the Al-doped carbon (10,0) nanotube.

It is visible, that the type of bonds of atom of aluminium with atoms of carbon very feebly influences quantity of energy levels. In comparison with a spectrum of basic model of the carbon (10,0) nanotube (Fig. 2) has occurred an acceptor level with energy -10.532 eV. Also there were splits of levels -9.636 and -9.148 eV. The parent of this split is spin multiplicity of the nanostructure doped by aluminium which quantity is equal to two.
It is necessary to note, that the nanostructure with aromatic bonds Al-C should be realized with greater probability as the nanostructure with single bonds Al-C is more on 10 kcal/mol.

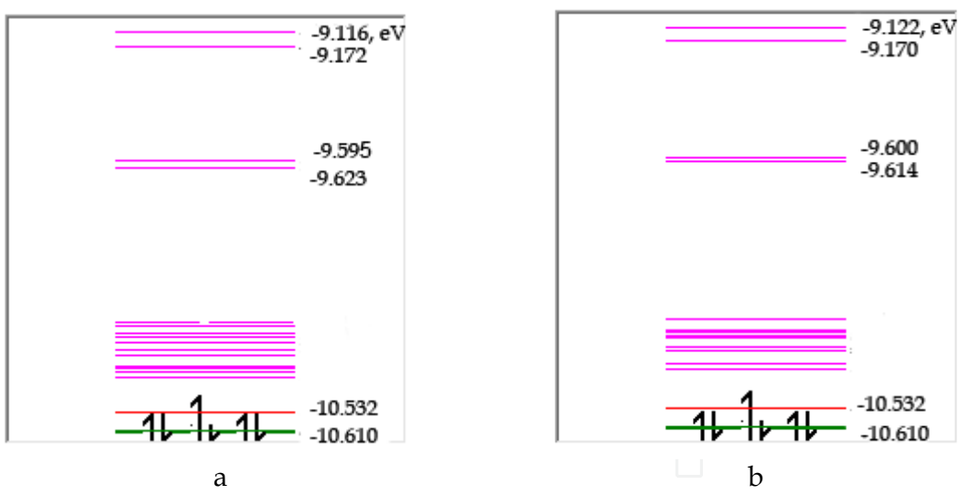

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Fig. 11. Energy band structure of a forbidden gap region of the Al-doped carbon (10,0) nanotube: (a) - aromatic bond Al-C; (b) - unary bonds Al-C.

Passivation of the Al-doped carbon (10,0) nanotube by hydrogen endings (Fig. 12a) renders appreciable influence on its energy distribution in the field of a forbidden gap (Fig. 12b). We see, that after passivation of edges of a nanotube by hydrogen in a forbidden region of a nanostructure some level by quantity -10.289 eV which visible is related to the defect created by impurity atom of aluminium was displayed.

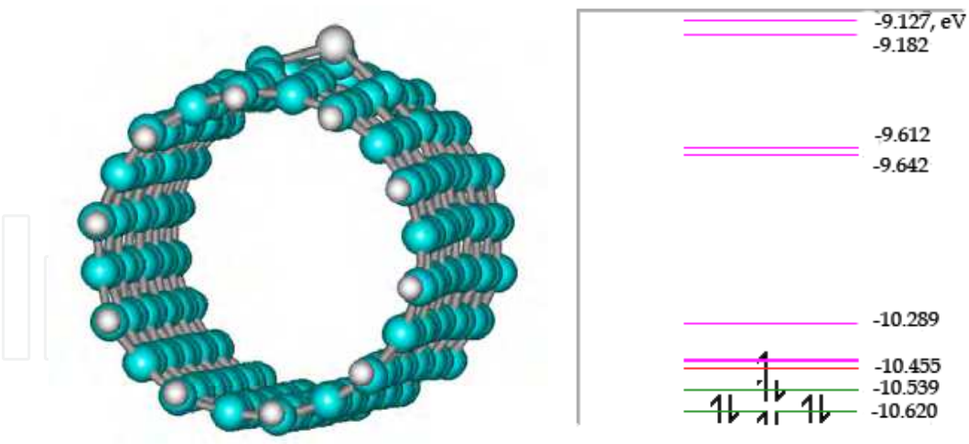

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Fig. 12. Al-doped carbon (10,0) nanotube with hydrogen endings: (a) - geometry of nanostructure; (b) - energy band structure of a forbidden gap.

2.5 Doping of a carbon (10,0) nanotube by atom of phosphorus

Doping of the carbon (10,0) nanotube by atom of phosphorus results in appreciable strain of geometry of a nanostructure (Fig. 13). It is related by that bonds C-P, having quantities 1.80, 1.80 and 1.79 Å, longer in comparison to typical length of bonds C-C, equal 1.41 Å. Besides the atom of phosphorus has on 0.3 E greater atomic radius than at atom of carbon that results in to its replacement for limits of a nanotube.

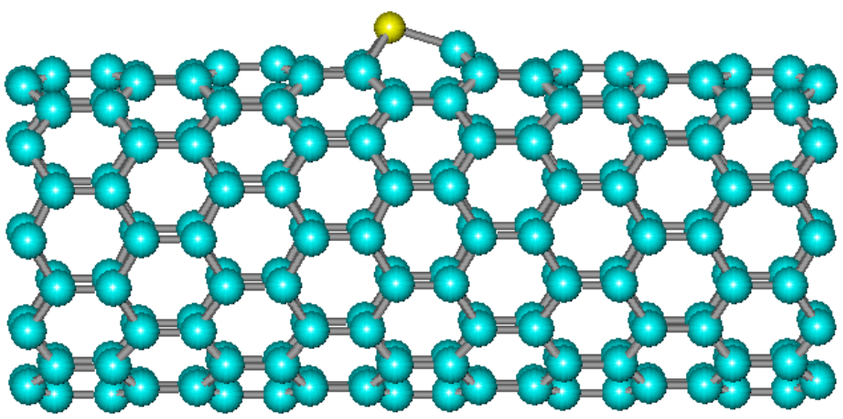

Fig. 13. Molecular mechanics model of the 200-atomic carbon (10.0) nanotube doped by atom of phosphorus.

It is necessary to note, that the atom of phosphorus shapes in a viewed nanostructure an essential lapse rate of mechanical stresses which value equally 0.05 kcal/(Å·mol). In a basic nanotube geometrical optimization is attained at a root-mean-square lapse rate equal 0.000001 kcal/(Å·mol).

The energy diagram of a viewed nanostructure is presented on Fig. 14. We see, that in a forbidden gap of the doped nanotube there was a level (-10.082 eV), which probably matches to the flaw created by atom of phosphorus.

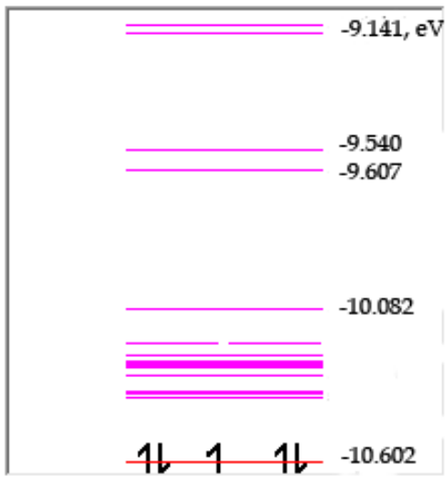

Fig. 14. Energy levels in a forbidden gap of the carbon(10,0) nanotube doped by atom of phosphorus.

The model of a phosphorus-doped (10,0) nanotube with hydrogen passivation of dangling bonds and its energy band structure are presented on Fig. 15. We see, that the geometry of a viewed nanostructure in the field of localization of atom of phosphorus after hydrogen passivation of dangling bonds on its edges has not changed.

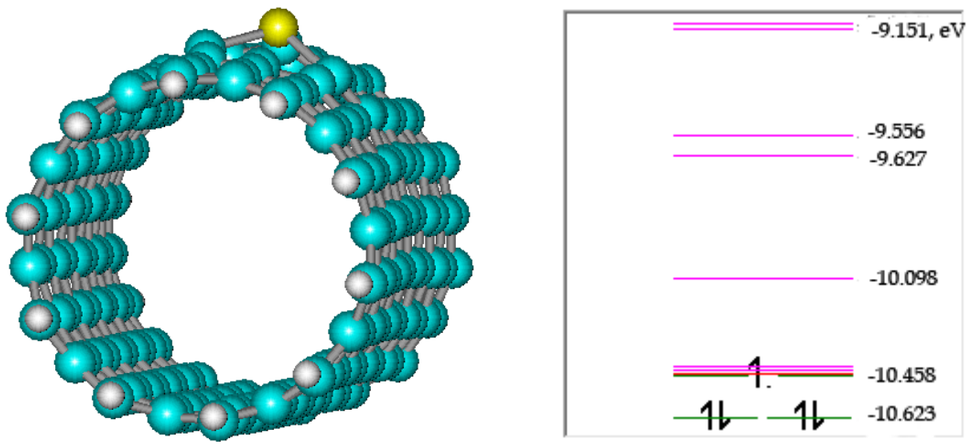

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Fig. 15. P-doped carbon (10,0) nanotube with hydrogen endings: (a) - geometry of the molecular mechanics model; (b) - Extended Hückel calculation of energies of orbitals.

In an energy distribution of a forbidden gap there were changes (Fig. 15b):
the upper filled level has risen up to quantity -10.46 эВ;
degeneration of some energy levels is removed;
quantities of energy levels have changed.

It is necessary to note, that the new level with energy -10.098 eV under effect of hydrogen endings has not changed the quantity.
The magnification of number of atoms of carbon in model of a phosphorus-doped nanotube up to 300 pieces results in to diminution of breadth of a forbidden gap and small bias of a new level up to quantity -10.11 eV.

3. Properties of doped carbon nanotube with indices (6,5)

3.1 Basic model of a carbon nanotube with indices (6,5)

There are many methods of model operation of those or other processes and structures. For nanotechnologies the method of the molecular mechanic model operation which basic element is the molecule well approaches. The separate atom too is considered as a molecule. In case of a nanotube the molecule is the nanotube. Atoms of a nanotube are foliated, featured by coordinates and type and also quantity of bonds.
Our model of nanotube consists from two hundred atoms of carbon, which geometrical optimization was led by method MM + with application the block-diagonal of the Newton-Raphson algorithm (Fig 16). The length of a nanotube is equated 22 Å, diameter - 7.3 Å. The distance between atoms is equated 1.41 Å. Chirality of the nanotube which it is well visible on figure, defined by its indices (6,5).
At model operation the applied aromatic bonds which well justify itself when atoms of carbon create rings as in this case. There is one more expedient of the plotting of bonds which total for atom of carbon should equate to four.
To calculation of energy properties of a nanotube we applied Extented Hückel Method (Hoffmann, 1963) without taking into account d-orbitals, with unit spin multiplisity and unweighted Hückel constant equal 1.75. Energy has made quantity equal -323263.1900 kcal/mol.

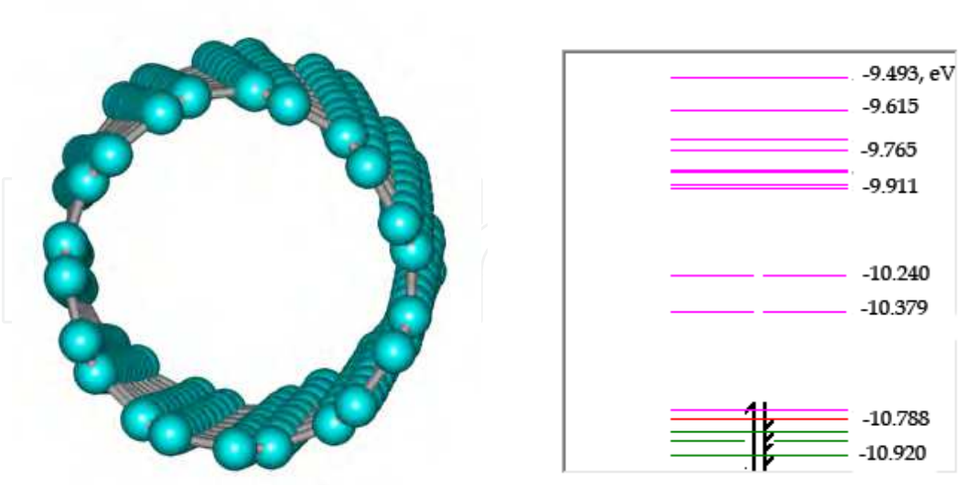

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Fig. 16. 200-atoms basic model (a) and energy-band structure (b) of a carbon nanotube with indices (6,5).

The energy-band structure of a basic nanotube (6,5) is presented on Fig. 16b. The upper filled level (HOMO 0), which is featured by orbital number 400, makes quantity -10.788 eV.

Energy of bottom of a conduction band is equated -9.91 eV. In fact the forbidden region has breadth equal 0.88 eV.
In a forbidden gap there is a series of levels which are caused by dangling bonds on edges of the nanotube. So, it is possible to apply atoms of hydrogen or nitrogen to passivation of the broken off bonds. On Fig. 17 passivation by atoms of hydrogen which are optimum in such cases is shown.

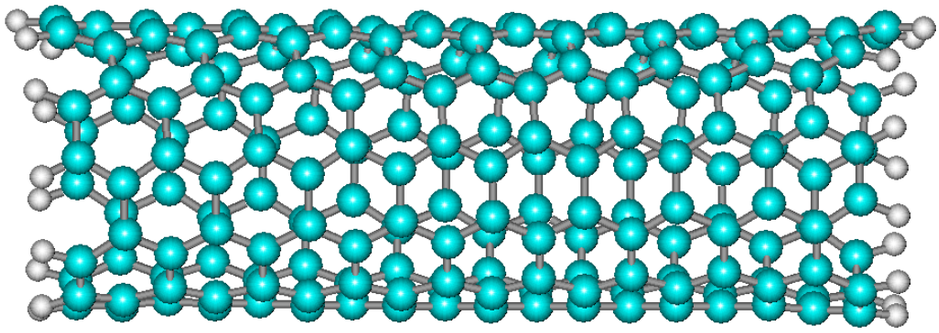

Fig. 17. Atoms of hydrogen fill dangling bonds on edges of the carbon (6,5) nanotube.

The energy of the nanotube with passivated ends has decreased to value -332889.25 kcal/mol that is caused by both H-atoms and a relaxation of a nanotube on edges where bonds have been broken off. The energy-band structure presented on Fig. 18a, considerably has changed in this case. The forbidden gap became clear from energy levels of the dangling bonds. Apparently from this figure, that the forbidden gap quantity is defined by a difference

$$\Delta E = E_{orb412} - E_{orb411} = 1.02 \text{ eV}.$$

The greater width of the gap is caused by a trace amount of carbon atoms.

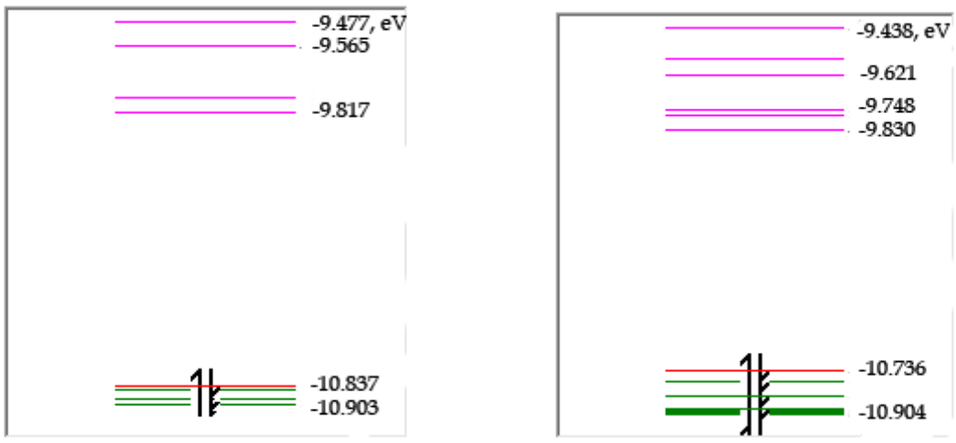

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Fig. 18. The energy-band structure of the base nanotube with indices (6,5) after passivation the dangling bonds by atoms of hydrogen: (a) - 200-atomic model; (b) - 400-atomic model.

The magnification of length of a nanotube twice results in to a raising of a ceiling of valence band on 0.1 eV, and the breadth of a forbidden region thus accordingly on as much decreases (Fig. 18b).

3.2. Doping carbon nanotube (6,5) by atom of boron

Doping of a carbon nanotube with indices (6,5) we shall carry out by replacement in the program of model operation of a nanostructure of the arbitrary atom of carbon by atom of boron. We exchange also aromatic bonds on single bonds, as boron trivalent. The nanotube (Fig. 19a) distorts in the field of localization of the alloyed atom of boron due to longer B-C bonds, equaled 1.65 Å, that on 0.24 Å it is more than for C-C bonds. Though the nuclear sizes of boron (1.17 Å) and carbon (0.91 Å) different enough, but covalent radiuses at them close enough, 0.82 and 0.79 Å, therefore the geometry of a tube is broken poorly. The energy-band structure of the B-doped nanotube (Fig. 19b) has a little changed in comparison with a spectrum of basic model (Fig. 16b):
degeneration of levels -10.240 and -10.379 eV is removed;
numerical values of other energy levels have a little changed.

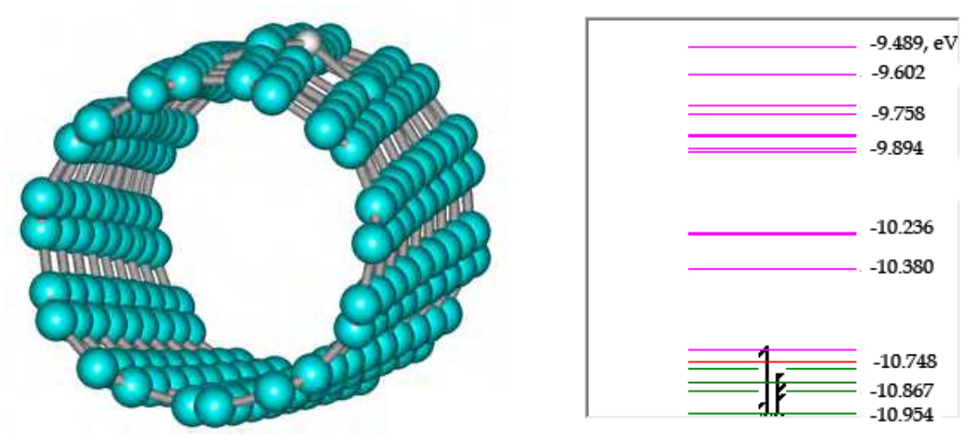

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Fig. 19. Geometry of the boron-doped carbon (6.5) nanotube (a) and its energy-band structure (b).

To passivation of dangling bonds on edges of a nanotube we shall apply hydrogen endings (Fig. 20a).
Apparently from Extended-Hückel calculations of the energy band structure diagram (Fig. 20b), that under effect of atom of boron and hydrogen passivation of dangling bonds the structure of the forbidden gap and its width which has become equal 0.898 eV (it was equal 1.03 eV) has changed. The local orbital the number 411 is filled only by one electron, as amount of valence electrons equally to eight hundred twenty one. It is acceptor with energy -10.71 eV (0,08 eV above valence band).
Thus atoms of carbon with numbers 157, 158 charged by the negative low fidelity equal charges on quantity 0.41e (e - electron charge), and the atom of carbon number 161 has negative charge 0.37e. The atom of boron has positive charge equal -0.66e.

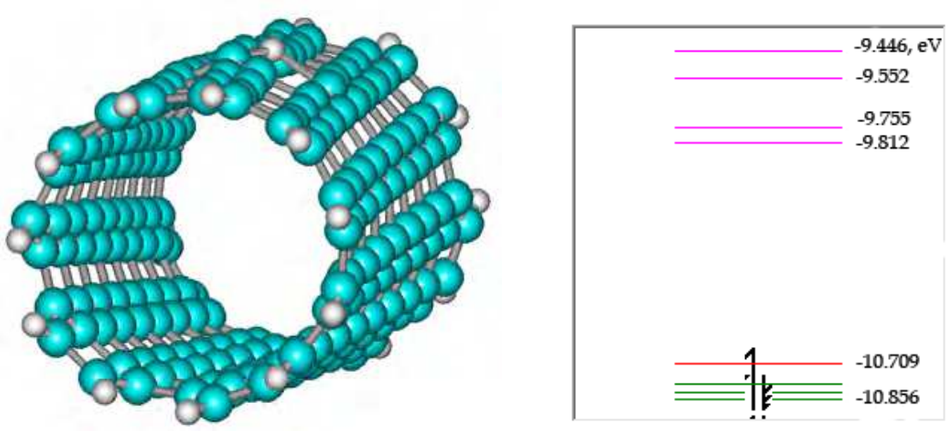

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Fig. 20. The B-doped carbon (6,5) nanotube with hydrogen endings: (a) - geometry of the nanostructure; (b) - energy band structure.

Thus around of atom of boron in a carbon nanotube complicated enough electronic pattern which corresponds to an orbital 411 and as which it is possible to term as acceptor local centre is created. It is necessary to note, that acceptor properties of this orbital can be realized at a heat (more than 900 K), as an energy level deep enough.

3.3 Doping carbon (6,5) nanotube by atom of nitrogen

For forming model of the N-doped carbon nanotube, we shall replace 163-rd atom of carbon with atom of nitrogen. The nanostructure does not distort almost under influence of the alloyed atom of nitrogen (Fig. 21) as lengths of bonds C-C and N-C differ feebly - 1.40 Å and 1.28 Å, accordingly.

Covalent and nuclear radiuses of atom of nitrogen are equaled 0.75 Å, i.e. smaller radiuse of atom of carbon which equal 0.77 Å and 0.91 Å, accordingly. In this connection, intensity around of atom of nitrogen is not minimal - the RMS gradient of mechanical stress is equal 0.0045 kcal/(Å·mol).

Total energy of the nanotube doped by nitrogen is calculated by Extended Hückel method and has made quantity -323849.25 kcal/mol. It is less than for the base nanotube which energy is equaled -323263.19 kcal/mol that speaks in the smaller sizes of radiuses and bonds of atom of nitrogen.

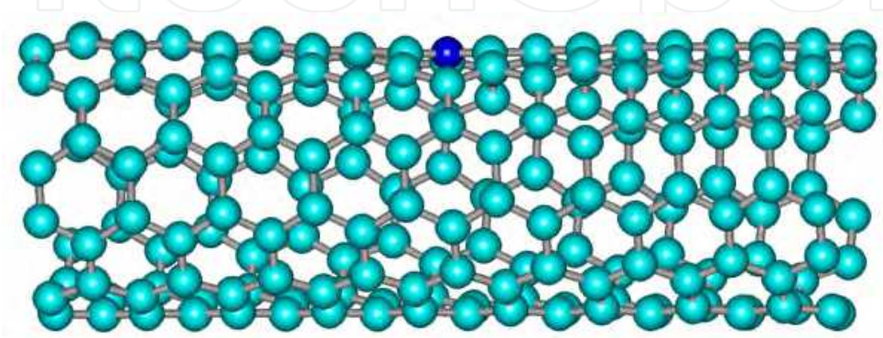


Fig. 21. Cross view of the nanotube with indices (6,5) doped by atom of nitrogen.

As we see on the diagram of energy spectrum of the nanostructure (Fig. 22), the fifth electron of atom of nitrogen has formed and has filled a level with energy -10.75 eV. On the one hand this level donor as it is filled by an electron and is level HOMO 0 (the highest among the levels filled by electrons), and from the second side - it is near to valence band and should be the acceptor. So it is necessary to consider this level as very deep donor level.The forbidden gap in case of presence of impurity of atom of nitrogen is defined by a difference ΔE =-9.92+10.79 =0.87 eV.

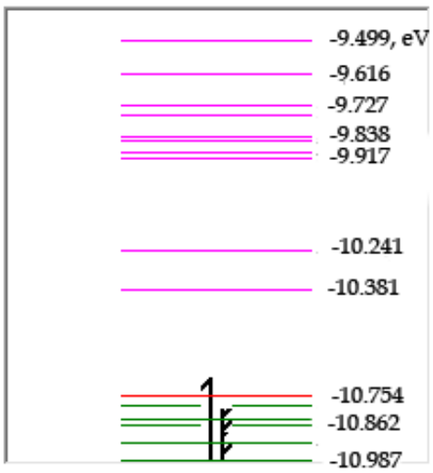


Fig. 22. Energy-band structure of a N-doped carbon nanotube with indices (6,5).

Also we see on Fig. 22 in a forbidden region there are some levels which are caused by the broken off bonds on edges of a nanotube. To neutralization of these levels we shall apply atoms of hydrogen (Fig. 23). Energy band diagram of the nanostructure in this case is shown on Fig. 24.

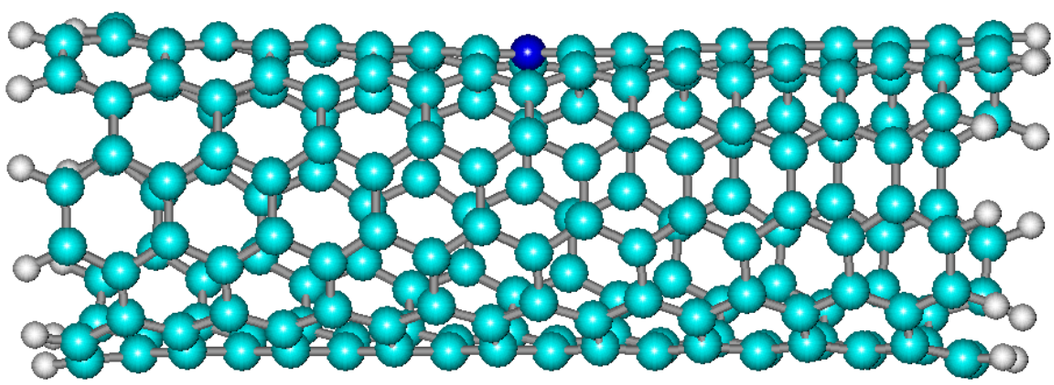


Fig. 23. Passivation of the torn off bonds on edges of the N-doped carbon (6,5) nanotube.

As we see on Fig. 24, the atom of nitrogen has formed occupied level with energy -9,829 eV, which is level HOMO 0 in this case.

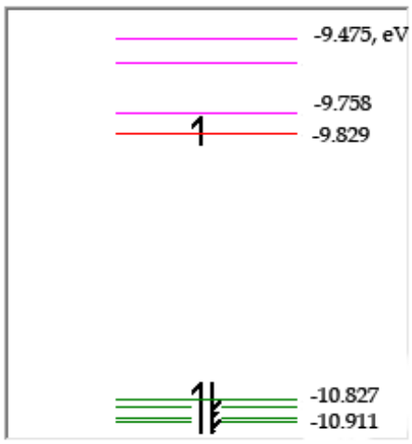


Fig. 24. Energy band diagram of the N-doped carbon (6,5) nanotube with hydrogen endings.

To term its donor it is impossible, as it deep enough (0.071 eV from level LUMO 0 with energy -9.758 eV). Presence of such energy level filled by an electron highly above valence band in the tubes alloyed by nitrogen should result in to improvement of their properties of electron emission.

3.4 Properties of the carbon (6,5) nanotube doped by atom of aluminium

For construction of model of the doped nanotube the 116-th atom of carbon on the atom of aluminium is replaceable in the program of its basic model. We shall replace also aromatic bonds of atom with atoms of carbon on unary. After embodying the given changes in the program and carryings out of geometrical optimization of a nanostructure, we shall receive model of the aluminium-doped carbon (6,5) nanotube (Fig. 25a). We see, that the nanotube essentially distorted under influence of the doped atom. It speaks the following parents:

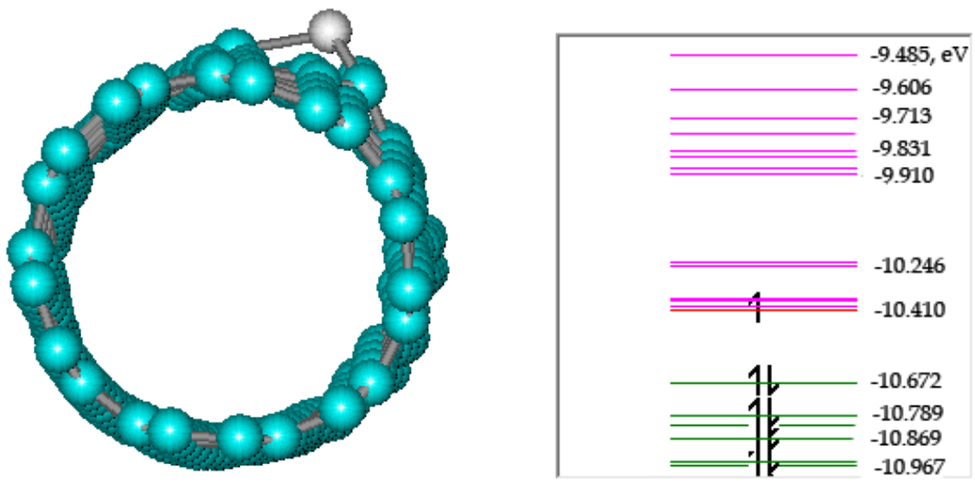
a) Atom of aluminium has twice greater radius (1.92 Å) than radius of atom of carbon (0.91 Å);
b) Covalent radius of atom of aluminium also greater than at atom of carbon, 1.18 Å against 0.77 Å;
c) Length of bonds C-Al which is equal 1.94 Å, is more than length of bonds C-C equal 1.41 Å.

It results in to that the atom of aluminium is pushed out of limits of the nanotube and its effective diameter increases up to quantity equal 8.51 Å.

Besides under influence of elastic forces of strain, atoms of carbon which are bound to atom of aluminium also are superseded from the optimum places and take new geometrical positions which are normal for the doped nanotube.

Extended Hückel calculation of energy of the aluminium-doped nanostructure yields value -322454.33 kcal/mol. It on 808 kcal/mol is more than for a basic (6,5) nanotube. Thus for doping a nanotube (6,5) by aluminium the significant energy is required.

The zone diagram of the Al-doped nanostructure in this case is shown on Fig. 25b. We see, that the orbital number 400 (HOMO 0) is filled half, hence, there was a vacant level with energy -10.41 eV. Thus, the atom of aluminium shapes an acceptor level near to valence band.



a b

Fig. 25. Al-doped carbon (6,5) nanotube: (a) - a dilatational view; (b) - an energy-band structure.

The nanostructure with hydrogen endings is shown on Fig. 26. Its Extended-Hückel energy is equaled -332121.573 kcal/mol. Electrical dipole moment of a nanotube, is equal 297.4 D - greater enough in comparison with a boron-doped nanotube (6,5).

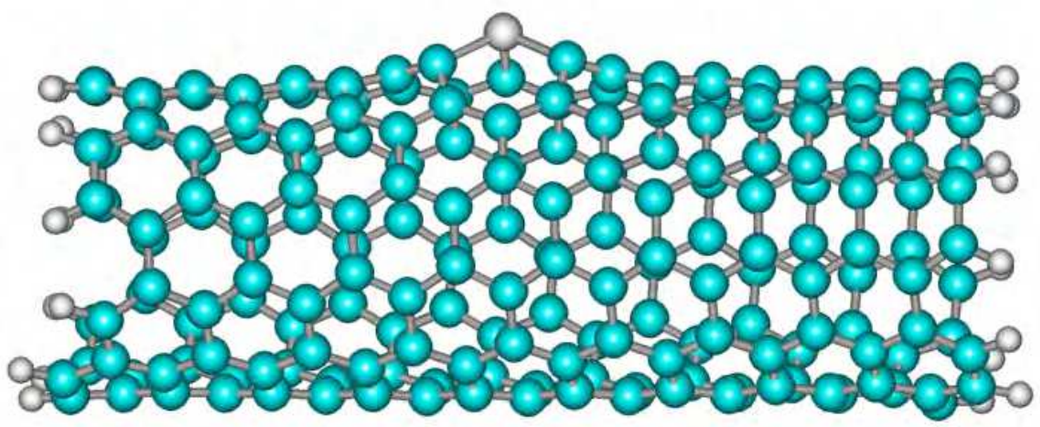


Fig. 26. Doped by atom of aluminium the carbon (6,5) nanotube with hydrogen endings.

Doping by atom of aluminium very strongly influences an energy band spectrum (Fig. 27) nanotubes that is related to its significant strain after doping, and also spin density of a nanostructure. In this case the impurity atom of aluminium creates an acceptor level (-10.373 eV) with an ionization energy equal 0.015 eV.

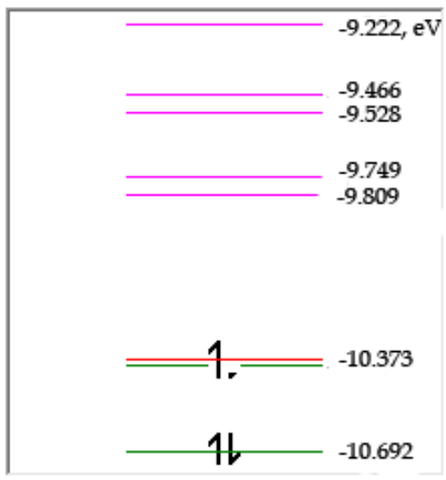


Fig. 27. Energy-band structure of the Al-doped (6,5) nanotube with hydrogen endings.

3.5 Doping by atom of phosphorus of a carbon (6,5) nanotube

The atom of phosphorus has five valence electrons, therefore it is necessary to expect occurrence in a nanotube of a donor centre near to it, as for aromatic bonds with atoms of carbon enough four electrons. We shall exchange in basic model of a 200-atomic nanotube the any atom of carbon with atom of phosphorus, having applied aromatic bonds C-P. For carrying out of geometrical optimization of the constructed P-doped nanostructure we shall use the molecular mechanic method MM + with application of the block-diagonal algorithm of Newton-Raphson. We shall gain model of the P-doped carbon (6,5) nanotube presented on Fig. 28. Apparently on pattern, that the atom of phosphorus has taken a place in exterior area near to a nanotube. It is caused by that bond C-P and atomic radius of phosphorus is more than bonds C-C and atomic radius of carbon on 0.4 and 0.3 Å, accordingly.

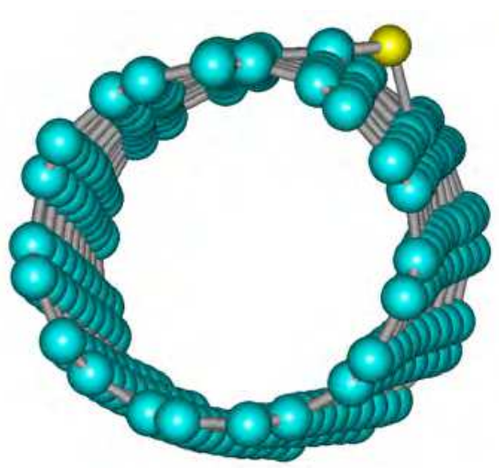


Fig. 28. The molecular mechanics model 200-atomic carbon (6.5) nanotube doped by atom of phosphorus.

In connection with mechanical stresses near to the impurity atom it is necessary to note, that the considered nanostructure is optimized only at RMS gradients of greater 0.015 kcal/(Å·mol), and for a basic nanotube analogous magnitude makes 0.000001 kcal/(Å·mol). The band diagram of a viewed nanostructure is presented on Fig. 29. Comparing the gained diagram with the diagram of a basic nanotube (Fig. 16b), we see, that the fifth electron of atom of phosphorus has occupied the free orbital 401 with an energy -10.758 eV and that in a forbidden region the level with an energy -10.082 eV was generated.

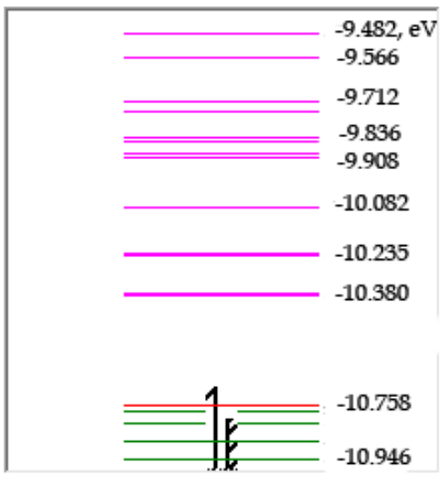
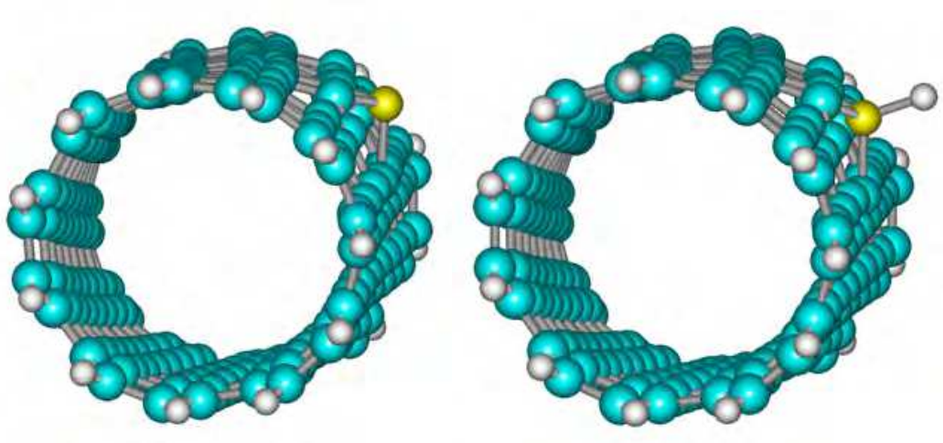


Fig. 29. Energy band structure of the 200-atomic carbon (6.5) nanotube doped by atom of phosphorus.

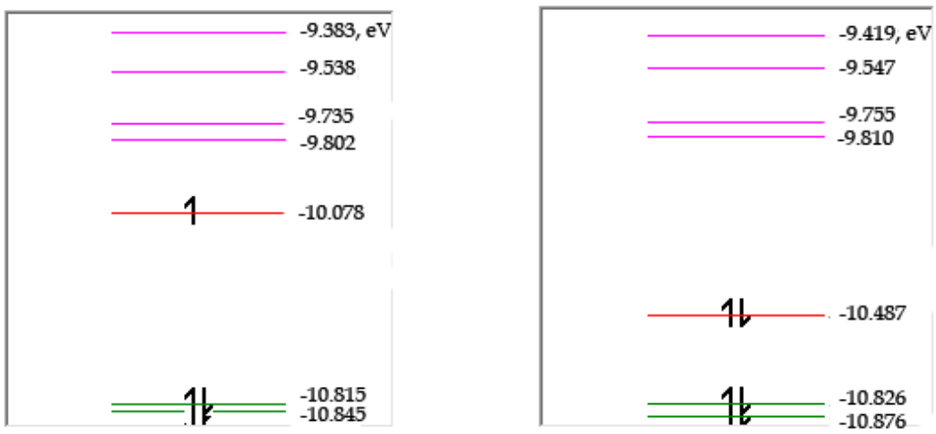
The models of a phosphorus-doped (6,5) nanotube with hydrogen passivation of dangling bonds is presented on Fig. 30.



a b

Fig. 30. Molecular mechanics models of the P-doped carbon (6,5) nanotube : (a) - hydrogen endings on edges of a nanostructure; (b) - the complete hydrogen endings.

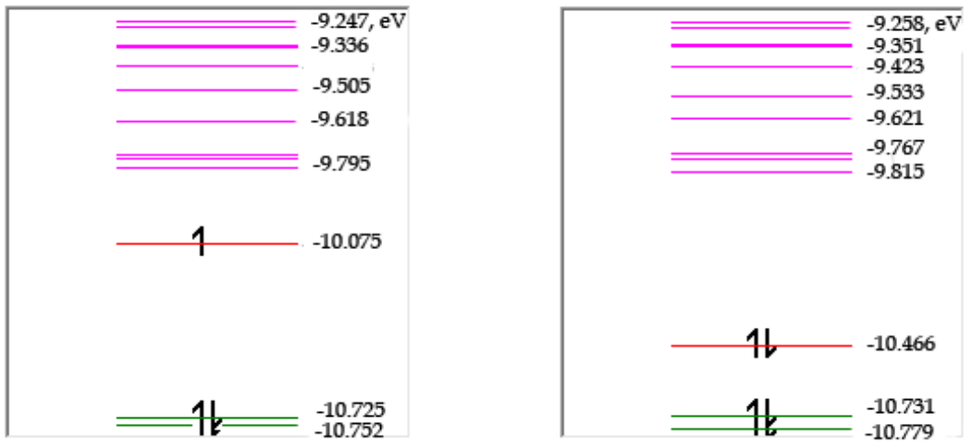
We see, that the doped nanotube has one broken off bond on atom of phosphorus. If such bond to leave without hydrogen passivation to it any other radical including the same nanotube can be affiliated.
Apparently on Fig. 31, passivation of the dangling bonds has essentially changed an energy distributions of a viewed nanostructure:
the upper filled levels have risen up to magnitudes -10.077 eV (a) and -10.487 eV (b);
degeneration of some energy levels is taken off;
quantities of energy levels have changed.



a b

Fig. 31. The phosphorus-doped 200-atomic carbon (6,5) nanotube: (a) - hydrogen endings on edges of a nanostructure; (b) - complete hydrogen endings.

The magnification of number of atoms of carbon in model of a phosphorus-doped nanotube up to 410 pieces results in to diminution of breadth of a forbidden gap and bias of a HOMO 0 levels up to quantities -10.466 eV (Fig. 32a) and -9.852 eV (Fig. 32b).



a b

Fig. 32. The phosphorus-doped 410-atomic carbon (6,5) nanotube: (a) - hydrogen endings on edges of a nanostructure; (b) - the complete hydrogen endings.

Thus, the impurity atom of phosphorus without hydrogen ending of its dangling bond can create in a nanotube a deep donor level with an ionization energy equal 0.28 eV. In case of when the free bond of atom of phosphorus is neutralized by atom of hydrogen the recombination centre is formed. Besides in any case, the impurity atom of phosphorus will reinforce emissivity of a nanotube as its valence electron occupies higher energy levels.

4. Conclusion

On models of semiconductor carbon nanotubes with chiral vectors (10,0) and (6,5), consisting of 200 atoms, effect of impurities of atoms Al, B, N and P on performances of their energy-band structure is viewed. The magnification of number of atoms of carbon of the doped nanostructure twice feebly influences its energy distribution, but results in to diminution of a forbidden gap of a nanotube approximately on 0.1 eV.

Process of doping of a carbon nanotube was simulated by replacement of one of its atoms of carbon on an impurity atom. Such doping of a nanotube in experiment can be implemented at existence of vacancies in it. Theories about equilibrium concentration of vacancies in nanotubes are not present, therefore it can become the purpose of the further developments.

It is necessary to note, that intercalation atoms in nanotubes can be viewed as interstitial atoms in crystals. Then their presence at a nanotube can determine process of doping also.

It is shown, that the energy distribution of levels in the field of a forbidden gap of the doped nanostructure strongly depends on passivation of its torn off bonds. In the present investigation modeling of process of such passivation was carried out by hydrogen endings.

Also it is shown, that doping of a carbon nanotube by atom of phosphorus results in to occurrence of dangling bond on its fifth valence electron, as for support of aromatic bonds with atoms of carbon enough four electrons. Passivation of this bond by atom of hydrogen results in to changes in an energy band structure of the doped nanotube.

Impurity atoms of boron and aluminium are representatives of the third group of a periodic system of elements, therefore they create similar acceptor levels in carbon nanotubes with chiral vectors (10,0) and (6,5):

a) atom of boron creates levels with activation energies 0.17 and 0.08 eV, accordingly;
b) atom of aluminium creates levels with identical activation energies 0.08 eV.

Atoms of nitrogen and phosphorus are representatives of the fifth group of a periodic system of elements, therefore it was expected, that they will create similar donor levels, but it has not proved to be true. The impurity atom of nitrogen creates in a carbon nanotube with a chiral vector (6,5) donor level with an ionization energy 0.07 eV, and in a nanotube (10,0) - very deep donor level near to valence band. The impurity atom of phosphorus creates in a carbon nanotube with a chiral vector (6,5) donor level with an ionization energy 0.28 eV, and in a nanotube (10,0) - very deep donor level near to valence band and a level with energy 10.1 eV.

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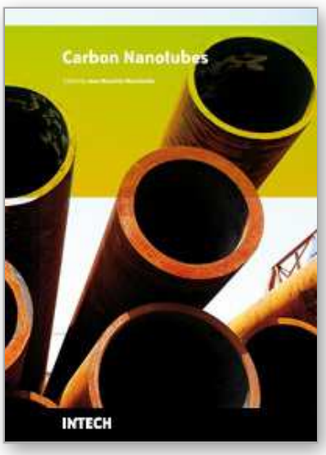

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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
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