

Atomic configuration, band structure and stability of fluorinated carbon nanotubes

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Abstract—The article discusses the model and the results of an ab initio calculation within the density functional theory of the band structure and fluorocarbon bond energy in different isomers of fluorine derivatives of single walled carbon nanotubes. The website developed for the generation of functionalized nanotubes' atomic configuration is presented. Also a system of seven geometrical parameters for the tube's geometry definition is proposed. Much attention is given to the changes in the electronic structure of carbon nanotubes due to the functionalization with fluorine. From the dependencies of the fundamental parameters (such as the band gap, Fermi energy and fluorocarbon bond energy) of the armchair and zigzag nanotubes on the diameter the corresponding values for graphene are estimated.

Keywords—carbon nanotubes, functionalization, fluorination, electronic structure, geometrical structure, generation, model, software.

I. INTRODUCTION

CARBON nanotubes (CNT) are considered to be one of the most promising materials for development of the electronics in the nanoregion [1]. In order to effectively utilize a material in micro- and nanoelectronics one needs to be able to control the material's electronic structure and the related parameters (in particular, the band gap). The techniques of modification of the electronic structure of single-walled CNTs (SWCNTs) may be divided into two groups: 1) without alteration of the physical structure of the SWCNTs (i.e. by applying an external electric field); 2) with modification of the SWCNTs' structure (i.e. by creating defects in the tube's atomic configuration). Among the techniques of the second group the chemical functionalization of walls and ends of CNTs takes a special place and may be considered an analogue to the doping of semiconductors. The functionalized CNTs represent a new class of nanomaterials with applications in both the composite materials and the nanoelectronic devices [2].

A rigorous research of the interactions between the CNT walls and different chemical elements (hydrogen [3], oxygen [4], nitrogen [5] and others) and compounds have been carried out during the last several years. Currently we may admit that fluorine appears to be one of the most interesting elements for the chemical functionalization of CNTs. Firstly, the chemistry of the fluorocarbon bond is well studied. Secondly, an experimental evidence of the possibility of fluorination of

CNTs has been obtained and the saturation stoichiometry C_2F has been found. [6, 7]

At this stage of the development of the technology the controlled production of F-CNTs with C_2F stoichiometry and predetermined structure is not achieved. Due to this reason the experimental investigation of their electronic structure is rather difficult. For the theoretical description of pure SWCNTs both the analytical [8] and numerical [9] approaches may be used. Since the geometrical structure of fluorinated SWCNTs is not known, their theoretical description appears to be more feasible with the use of computational methods.

The work by Kudin et al. [10] has proposed four possible isomers of fluorinated SWCNTs with C_2F stoichiometry (A – D on Fig. 1). Using the density functional theory approach in two approximations the authors have calculated the band gap and the Fermi level for tubes (10, 10) and (18, 0). It was confirmed that the bond energy and electronic structure parameters vary between different isomers. Later on it was found that fluorination not only changes the electronic structure of SWCNTs but also alters their geometry. [11]

In Ref. [12] Ranjan and Seifert investigated the transport properties of fluorinated SWCNTs (10, 10) (isomer A) and (10, 0) (isomer C) within the density functional theory. They have found that both fluorinated SWCNTs have metallic conductivity. The electronic structure and the band gap for F-SWCNT (10, 0) of isomers B – D were studied by Seifert et al. [13] According to their results the band gap equals 4 eV for isomer B, 0 eV for isomer C and 1 eV for isomer D.

Thus, the fluorine functionalization leads to alteration of the electronic structure of single-walled carbon nanotubes and may turn a metallic nanotube into a semiconducting one and vice versa. So far the electronic structure of the F-SWCNTs is not sufficiently studied. Due to the fact that the results of the ab initio calculations of the electronic structure are available only for several nanotubes (mostly, the primitive ones), the investigation of the properties of a wide range of SWCNTs appears to be interesting both fundamentally and practically.

II. METHODOLOGY

From the five isomers depicted on Fig. 1 not all are available in the armchair and zigzag nanotubes with arbitrary chirality indices. In particular from the symmetry consideration standpoint the chirality index is required to be even for isomers D, E of the armchair and for isomers C, D of the zigzag tubes. In order to calculate the properties of the isomers

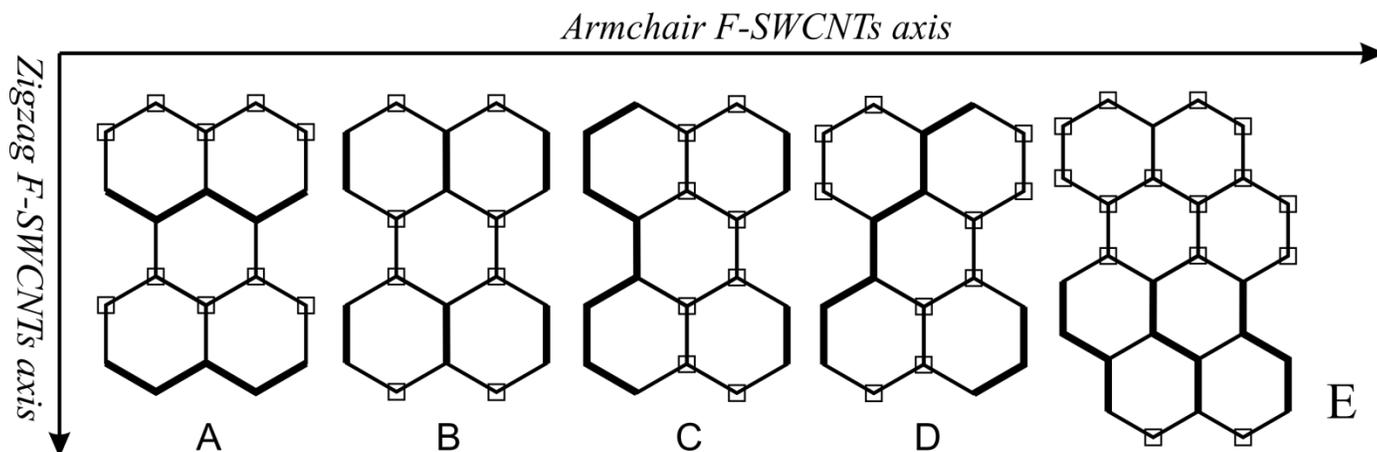


Fig. 1. Isomers of the achiral F-SWCNTs with C_2F stoichiometry. Squares denote fluorinated carbon atoms.

C, D of the armchair and the isomers D, E of the zigzag nanotubes the unit cell must be replicated along the CNT axis. However the isomers A and B do not impose any restrictions on the set of the tubes studied and for this reason we consider only these isomers in the present paper.

The calculation was carried out within the density functional theory in local spin-density approximation and 6–31G basis set which uses 6 primitive gaussian functions to represent each of the core atomic orbitals and each of the valence orbitals is composed of two basis functions (which in turn consist of three and one primitive gaussian functions). The density functional theory (DFT) was chosen because it is known to be a very efficient tool for investigation of the properties of molecules with up to hundreds of atoms. This theory is thoroughly tested and widely applied for studying the nanoobjects. [14–16] During the calculation we used the resources of the Computing center of the Voronezh State University and the Gaussian software package [17].

We used periodic boundary conditions (the nanotubes were approximated to be infinite) for 200 points in the Brillouin zone.

The electronic structure and the related parameters (the energy band gap, the Fermi energy and the ionization energy) were investigated for zigzag nanotubes of chiralities from (0, 3) to (0, 17) and armchair nanotubes of chiralities from (3, 3) to (15, 15). The band gap was calculated as the difference between the energies of the lowest unoccupied crystal orbital (LUCO) and the highest occupied crystal orbital (HOCO). In the further text we shall use the term “crystal orbital” instead of “molecular orbital”, since the calculation was carried out for the infinite CNTs and the wave functions were approximated by the Block waves. The Fermi energy was estimated as the HOCO energy for the metallic nanotubes and as the energy corresponding to the middle of the band gap for the semiconducting nanotubes. Also we have estimated the ionization energy of the F-SWCNTs as the HOCO energy (according to the DFT version of the Koopmans theorem [18]).

In order to account for the curvature effects occurring in the nanotubes of the small diameters we have used a cylindrical model of the unit cell in the calculation.

The method was tested in the calculation of the band structure of pristine carbon nanotubes and the comparison of the data obtained with the theoretical (both analytical [19] and numerical [20, 21]) and experimental [22, 23] data was carried out with satisfactory results [24].

The fluorocarbon bond length was taken to be 1.35 Å [25, 26]. The fluorine atoms connected the nanotube walls from the outer side. In the calculation the geometric structure was optimized to the minimum of the total energy.

III. GENERATION OF INPUT FILES

In order to generate input files for the Gaussian suite of programs we have developed special software. This software allows the generation of structure description files for isomers A and B of F-SWCNTs with arbitrary chirality indices.

As it may be shown the full description of geometric structure of an ideal pure achiral SWCNT in the molecular coordinate system may be achieved with just 3 parameters (for example, two bond lengths (for the C–C bonds parallel and not parallel to the tube’s axis) and the translational vector length).

Considering the isomers A and B of an ideal achiral functionalized SWCNTs we have shown that the description of their geometric structure requires a system of 7 geometric parameters.

Let’s denote functionalized carbon atoms as C_2 and not-functionalized carbon atoms in F-SWCNTs as C_1 . Let’s also denote the functional atoms as F. Then we may use the following values to fully describe the geometric configuration of F-SWCNTs in the molecular coordinate system:

- 1) L_{11} – bond length C_1-C_1 ;
- 2) L_{12} – bond length C_1-C_2 ;
- 3) L_{22} – bond length C_2-C_2 ;
- 4) D_1 – diameter of the circumcircle of the polygon, formed by the atoms C_1 , belonging to the same plane (Fig. 2);
- 5) D_2 – diameter of the circumcircle of the polygon, formed by the atoms C_2 , belonging to the same plane (Fig. 3);
- 6) *Angle* – angle between three atoms $C_1-C_2-<F>$ (for isomer A) and $C_2-C_2-<F>$ (for isomer B);
- 7) L_{2F} – bond length C_2-F .

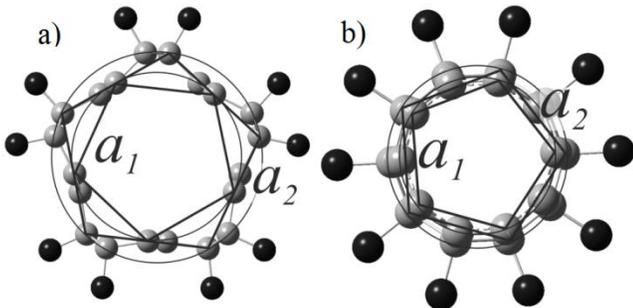


Fig. 2. Definition of the diameters D_1 , D_2 for isomer A of armchair (a) and zigzag (b) F-SWCNTs.

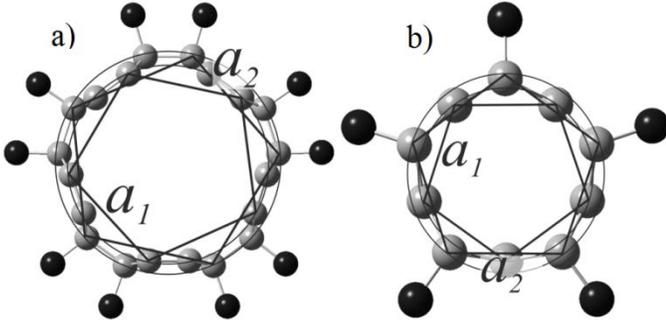


Fig. 3. Definition of the diameters D_1 , D_2 for isomer B of armchair (a) and zigzag (b) F-SWCNTs.

It may be proven that these 7 parameters fully define the SWCNTs' geometry in the unit cell. This leads to an important conclusion that once we find the dependency of these parameters on the diameter of the SWCNTs, we may extrapolate the dependency in the region of large diameters and thus generate the best fitting geometric configurations for nanotubes with many atoms in the unit cells. This in turn allows us to reduce the calculation time greatly.

We shall provide the full generation algorithm and the derivation of the atomic coordinates and translational vector length from the seven parameters listed above elsewhere. It is worth noting that the online interface of the software is available at <http://www.alexganin.com/en/FcncGenerator>.

Current version of the software supports several modes.

Optimized.

In this mode the software uses data of the system parameters, calculated as a result of optimization of the geometrical structure of the SWCNTs, functionalized with fluorine atoms in the Gaussian 03. That is why only certain SWCNTs for which the data is known are available for the generation. Besides, in this mode only fluorine is accepted as the functional element.

Not optimized.

Only carbon-carbon and fluorocarbon bond lengths (L_{CC} and L_{CF} respectively) are specified. The other parameters correspond to those in the ideal SWCNTs. Thus, denoting the chirality indices n , m , we obtain:

$$L_{11}, L_{12}, L_{22} = L_{CC} \quad (1)$$

$$D_1, D_2 = L_{CC} \frac{\sqrt{3(n^2 + nm + m^2)}}{\pi} \quad (2)$$

$$L_{2F} = L_{CF} \quad (3)$$

The *Angle* is taken to be 90°

Custom.

In this mode the user may specify arbitrary values for the parameters used in the generation of functionalized SWCNTs. The correct results are not guaranteed for this mode.

IV. ELECTRONIC STRUCTURE

During optimization of the geometric structure of unit cells of isomers A and B of achiral F-SWCNTs to the minimum of the total energy it was found that the fluorination leads to qualitative changes in the atomic configuration of the nanotubes which can be explained as a consequence of two factors: 1) mutual repulsion of partially negatively charged fluorine atoms; 2) orientation of the chemical bonds in functionalized carbon atoms to the vertices of a tetrahedron. Changes in geometric structure and symmetry of the SWCNTs unit cells are followed by radical changes in the electronic structure of the tubes. And depending on the chirality of the CNT and the isomer we may observe transitions from the metallic conductivity to the semiconducting and vice versa. Moreover, we have found that one of the consequences of fluorination is lowering of the Fermi energy of the CNTs by 2 – 3 eV. The tables 1, 2 summarize the data on the changes of the parameters of the SWCNTs' electronic structure caused by fluorination.

Table 1. Changes of the electronic structure parameters in zigzag SWCNTs as a result of fluorination. Letters M, S denote metallic and semiconducting conductivities respectively: the first letter applies to the pristine SWCNT and the second one to the F-SWCNT. Only the second chirality index m is shown since the first one is taken to be zero.

m	Isomer A			Isomer B		
		ΔE_g (eV)	$\Delta E_F $ (eV)		ΔE_g (eV)	$\Delta E_F $ (eV)
3	M – S	1.792	1.22	M – S	0.179	2.13
4	M – S	0.837	1.50	M – M	0.000	2.24
5	M – S	1.536	1.84	M – S	0.400	2.53
6	M – M	0.000	1.89	M – S	0.511	3.17
7	S – S	1.456	2.03	S – S	0.558	3.13
8	S – M	-0.785	2.11	S – S	0.206	3.32
9	M – S	1.476	2.48	M – S	1.051	3.63
10	S – M	-0.755	2.54	S – S	0.480	3.61
11	S – S	0.346	2.69	S – S	0.394	3.76
12	M – M	0.000	2.71	M – S	1.376	3.75
13	S – S	0.455	2.78	S – S	0.826	3.78
14	S – M	-0.742	2.90	S – S	0.726	3.84
15	M – S	0.881	2.93	M – S	1.489	3.87
16	S – M	-0.534	2.96	S – S	1.016	3.87
17	S – S	0.196	3.04	S – S	0.975	3.92

As it is obvious from the table 1, we can establish a conductivity classification rule for the isomer A of zigzag F-SWCNTs: if the chirality index is even then the conductivity is metallic; if the chirality index is odd then the conductivity is

semiconducting. The only exception to this rule is F-SWCNT (A) (0, 4) which is semiconducting.

Table 2. Changes of the electronic structure parameters in armchair SWCNTs as a result of fluorination. Letters M, S denote metallic and semiconducting conductivities respectively: the first letter applies to the pristine SWCNT and the second one to the F-SWCNT. Only the second chirality index m is shown since the first one is the same.

m	Isomer A			Isomer B		
		ΔE_g (eV)	$ \Delta E_F $ (eV)		ΔE_g (eV)	$ \Delta E_F $ (eV)
3	M – M	0.000	2.72	M – S	2.746	2.57
4	M – M	0.000	3.47	M – S	1.915	3.21
5	M – M	0.000	3.50	M – S	1.828	3.42
6	M – M	0.000	3.64	M – S	1.578	3.65
7	M – M	0.000	3.65	M – S	1.589	3.72
8	M – M	0.000	3.71	M – S	1.489	3.83
9	M – M	0.000	3.72	M – S	1.505	3.86
10	M – M	0.000	3.75	M – S	1.469	3.92
11	M – M	0.000	3.75	M – S	1.493	3.94
12	M – M	0.000	3.76	M – S	1.456	3.98
13	M – M	0.000	3.75	M – S	1.470	3.99
14	M – M	0.000	3.77	M – S	1.449	4.01
15	M – M	0.000	3.77	M – S	1.463	4.02

This rule can be qualitatively understood by considering the electronic structure of the zigzag F-SWCNTs (isomer A) (Fig. 4, b). One may notice that the energetic level corresponding to the HOCO of the F-SWCNTs (A) is fourfold degenerate (including the spin related degeneracy). And for F-SWCNTs (A) with even chirality indices this orbital is occupied only halfway, whereas for the SWCNTs with odd chirality indices it is fully occupied. The exception of the (0, 4) tube is explained by the decrease of the degeneracy of the HOCO to the twofold (what leads to the full occupation of the energetic level under consideration and opening of a non-zero band gap).

Typical band diagrams for simple armchair and zigzag F-SWCNTs (0, 5) and (5, 5) of both isomers are provided on figures 4, 5. Thus, we conclude that all semiconducting F-SWCNTs studied have direct band gaps.

Moreover as it is noticeable from the table 1 all zigzag F-SWCNTs fluorinated in B pattern are semiconducting.

As it is shown in the table 2 armchair F-SWCNTs (isomer A) retain their metallic conductivity, whereas for the armchair SWCNTs fluorinated in B pattern we observe the transition to the semiconducting state. It is also obvious from the table that the band gap is decreasing with the diameter and chirality of the nanotubes in question.

Now let us consider the dependencies of the fundamental parameters of the electronic structure of the F-SWCNTs from their diameter and chirality. On the Fig. 6 the dependency of the band gap on the diameter of the zigzag semiconducting fluorinated SWCNTs (isomer A) is provided. It is noticeable that with the increase of the diameter E_g decreases. This fact

lies in accordance with the fact that all armchair F-SWCNTs of this isomer are metallic and testifies that isomer A of fluorinated graphene is likely to be metallic. The Fig. 7 gives the dependency of the band gap on the diameter of the isomer B of the achiral F-SWCNTs. From the plot one may see that on the contrary to all previously considered types of nanotubes (including pristine ones) the band gap of zigzag F-SWCNTs (isomer B) grows with the diameter. The stabilization of this growth occurs at the value of 1.5 eV. In the case of the armchair F-SWCNTs the band gap decreases with diameter. The stabilization of this decrease occurs on the value of 1.5 eV as well. By analyzing the dependencies on the fig. 4 we may expect the band gap of the graphene fluorinated in the B pattern to have a magnitude of 1.5 eV. This result is confirmed by the data on the band gap of the zigzag and armchair F-SWCNTs and testifies in favor of validity of the calculation.

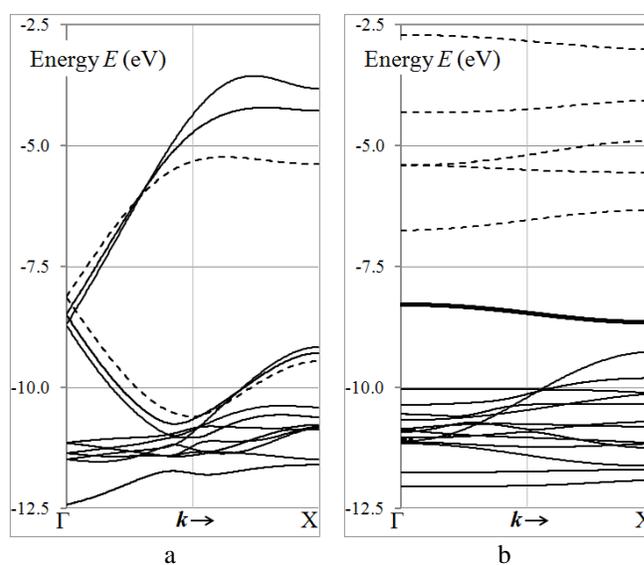


Fig. 4. Electronic structures of the armchair F-SWCNT (5, 5) (a) and zigzag F-SWCNT (0, 5) (isomer A).

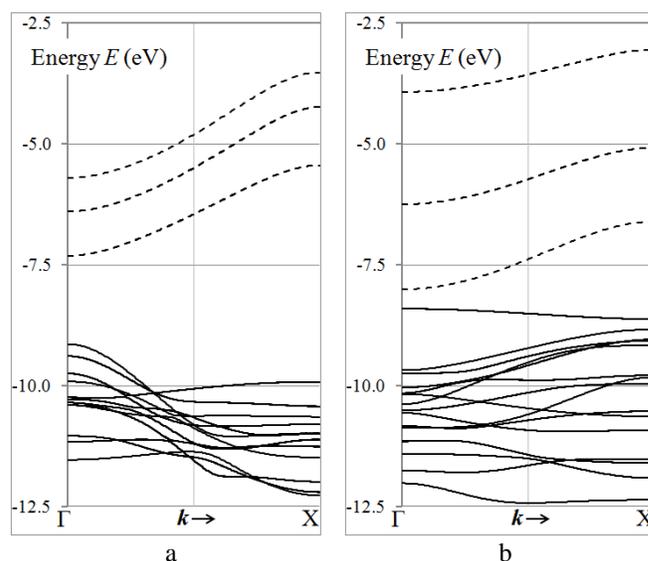


Fig. 5. Electronic structures of the armchair F-SWCNT (5, 5) (a) and zigzag F-SWCNT (0, 5) (isomer B).

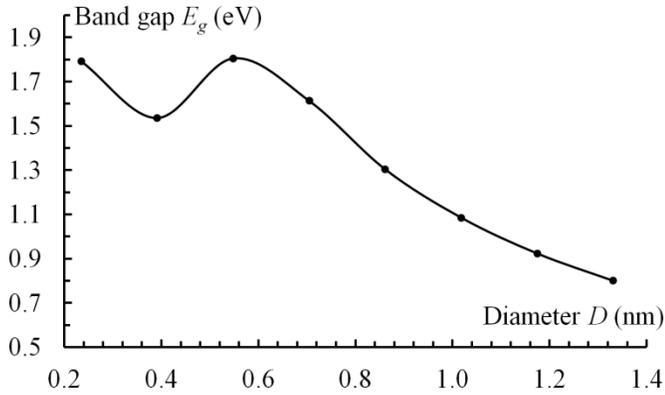


Fig. 6. Dependency of the band gap E_g on the diameter D of the zigzag semiconducting F-SWCNTs (isomer A).

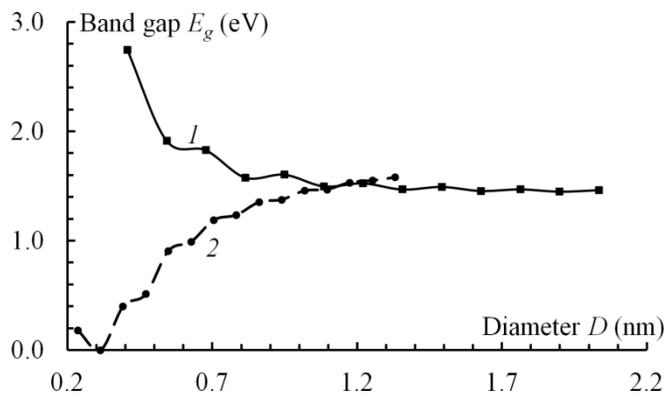


Fig. 7. Dependencies of the band gap E_g on the diameter D of the isomer B of armchair (1) and zigzag (2) F-SWCNTs.

The results obtained for the Fermi level energy and the ionization energy shown on the Fig. 8, 9 are also of certain interest.

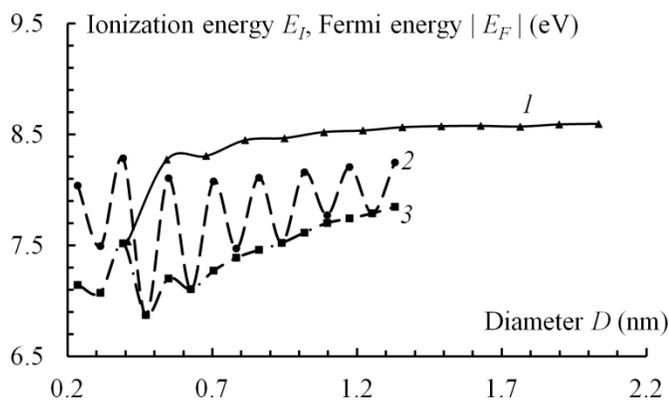


Fig. 8. Dependencies of the modulus of Fermi energy $|E_F|$ and the ionization energy E_I on the diameter D of the isomer A of achiral F-SWCNTs: 1 – $|E_F|$ and E_I of the armchair F-SWCNTs; 2 – E_I of the zigzag F-SWCNTs; 3 – $|E_F|$ of the zigzag F-SWCNTs.

As it is well known from the theoretic [27] and experimental [28] studies the Fermi level in the carbon

nanotubes lies at the value of $-5.2 - -4.8$ eV. As it is noticeable from the figures 8, 9 in the fluorinated SWCNTs it is significantly lower. The general tendency of the ionization energy and the modulus of the Fermi energy is to increase with the diameter in the region of small diameters and change insignificantly in the region of larger diameters. On the contrary, the modulus of the Fermi energy and the ionization energy of pristine tubes do decrease with the diameter in the region of $D < 1.0$ nm and do not change with the diameter for larger diameters. From the experiments involving fluorination of SWCNTs it is known that, generally, fluorine atoms do not distribute evenly all along the SWCNT but rather tend to form fluorinated zones. This phenomenon opens opportunities for creation of different structures of lowered dimensionality based on the partially fluorinated SWCNTs (for instance, quantum dots).

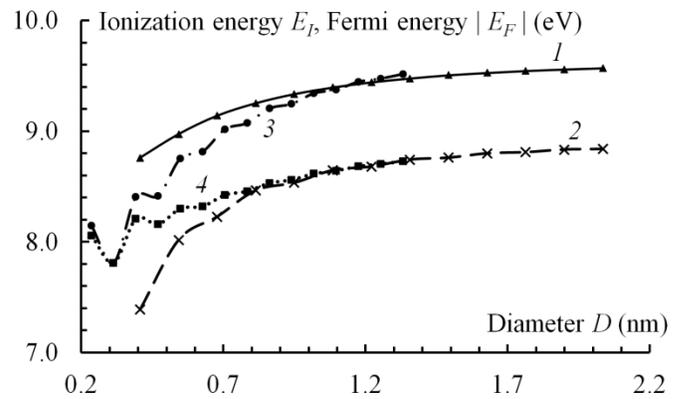


Fig. 9. Dependencies of the modulus of Fermi energy $|E_F|$ and the ionization energy E_I on the diameter D of the isomer A of achiral F-SWCNTs: 1 – E_I of the armchair F-SWCNTs; 2 – $|E_F|$ of the armchair F-SWCNTs; 3 – E_I of the zigzag F-SWCNTs; 4 – $|E_F|$ of the zigzag F-SWCNTs.

V. STABILITY OF F-SWCNTS

The last section of this paper focuses on the estimation of bond energy in fluorinated carbon nanotubes which we carried out based on the results of the calculation.

The fluorocarbon bond energy was estimated following the approach first shown in works of Ewels et al. Firstly, we calculated the bond energy of pure F-SWCNTs E_{total}^{CNT} . After that we calculated the total energy of fluorinated F-SWCNTs E_{total}^{F-CNT} . Then the fluorocarbon bond energy was determined using the following formula:

$$E_b^{C-F} = \frac{E_{total}^{F-CNT} - E_{total}^{CNT}}{N^F} - E_{total}^F \quad (4)$$

Here

$$E_{total}^F = E_{total}^{F_2} / 2 \quad (5)$$

And $E_{total}^{F_2}$ represents the total energy of F_2 molecule. N^F is the number of atoms in the F-SWCNT's unit cell.

Let us investigate the dependency of the E_b^{C-F} on the diameter and chirality of the tubes. The results obtained are in good agreement with results of Ewels from Ref. [29] for F-

SWCNT (8, 8) (A). The dashed lines on the picture correspond to the estimated fluorocarbon bond energy in graphene for isomers A and B. We suppose that dependencies for the E_b^{C-F} of armchair and zigzag F-SWCNTs converge to two values which we interpret as bond energies for graphene. Thus, the bond energy in fluorinated graphene (A) is 1.2 eV per bond and 1.0 eV for fluorinated graphene (B).

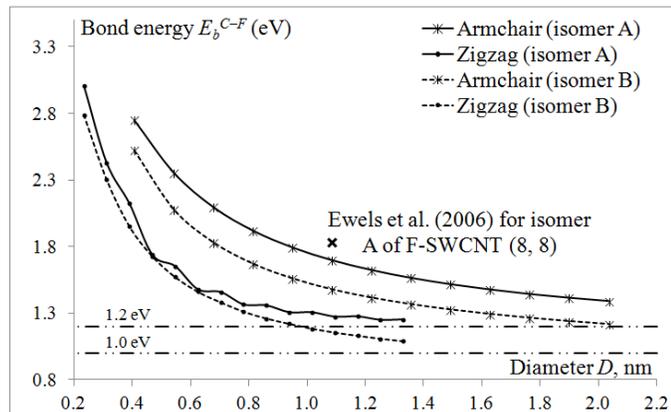


Fig. 10. The obtained dependencies for bond energy in armchair and zigzag F-SWCNTs (for isomers A and B).

CONCLUSION

We have investigated the electronic structure and the related parameters of two isomers of fluorinated armchair (with chirality indices from (3, 3) to (15, 15)) and zigzag (with chirality indices from (0, 3) to (0, 17)) single-walled carbon nanotubes with C_2F stoichiometry. The results obtained allow us to propose a broad range of possible applications for partially fluorinated SWCNTs. The examples of those applications include metal-semiconductor contacts, quantum wells and dots and others. The developed website and software for carbon nanotubes' atomic configuration generation provide researchers with important tools to investigate not only the properties of fluorinated achiral nanotubes but also the properties of achiral nanotubes functionalized with any chemical element (and without functionalization at all). The introduced system of seven geometrical parameters for atomic configuration definition might be proven useful for systematization of data on the SWCNTs' geometry.

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