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To cite this article: M E Belenkov *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **537** 022058

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Simulation of the structure and electronic properties of fluorographene polymorphs formed on the basis of 4-8 graphene

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Abstract. As a result of a theoretical analysis of the possible structure of polymorphic varieties of compounds obtained from the fluorination of L_{4-8} graphene, the possibility of existence of 6 main structural varieties of $CF-L_{4-8}$ layers is established (T1-T6 structural types). Ab initio calculations of these layers were performed by the density functional theory method using the generalized gradient approximation. As a result of the calculations, it was established that only five polytypes have a stable structure except for the T3 type layer. The crystal lattices of $CF-L_{4-8}$ compounds are tetragonal for the T1 - T5 types, and for the T6 type crystal lattice is orthorhombic. The sublimation energies of $CF-L_{4-8}$ polymorphs of fluorographene vary in the range of 13.36 to 14.09 eV/(CF), which is slightly less than the calculated value of this parameter (14.32 eV/(CF)) for experimentally synthesized $CF-L_6$ fluorographene of T1-type. The maximum band gap, equal to 4.96 eV, is observed for the T2 type layer, and the minimum value (3.05 eV) corresponds to the fluorographene layer of the T3 type.

1. Introduction

The formation of graphene compounds with various non-carbon atoms and molecular groups allows modifying their properties, so that instead of metallic, its properties become semiconducting. Functionalization of graphene is possible by hydrogen, chlorine, oxygen, fluorine atoms, OH, NH_2 molecular groups and others [1-6]. Among the various compounds based on graphene, fluorographene appears to be the most promising. This is linked to thermal stability and high uniformity of properties of graphene functionalized by fluorine [7-11]. The possibility of the existence of a number of different structural varieties of fluorographene differing in the way of attaching fluorine atoms to layers of hexagonal graphene is theoretically predicted [12-14]. These polymorphic varieties of fluorographene should have different electronic properties, which is of interest for practical applications in electronics. It is possible to extend the range of variation of the properties of fluorographene compounds if the non-hexagonal polymorphic graphene varieties described in papers [15-17] are used as the basis for their synthesis. In this paper, a theoretical study of the structure and electronic properties of fluorographene compounds that can be formed on the basis of the graphene layer L_{4-8} is performed.

2. Methods

The possible structure of polymorphic varieties of fluorographene compounds formed during the chemical adsorption of fluorine on L_{4-8} graphene was examined in the case of the addition of fluorine



atoms on both sides of the graphene layer. The addition of non-carbon atoms only from one side of the layer leads to the formation of nanotubes with the structure of the scroll, so this case was not considered [18,19].

As a result of analysing possible methods of attachment, it was found that there are six main ways of attaching non-carbon atoms to 4-8 graphene. The main structures are characterized by the fact that in all of them carbon atoms are in equivalent structural states. The images of these structures are shown on figure 1. Since the fluorographene, experimentally synthesized on the basis of L_6 graphene, has structural type marked earlier as T1, a similar method of attaching fluorine atoms to the L_{4-8} layer of graphene was also marked as T1. The structure of T1 type is characterized by the fact that if we examine a carbon atom to which a fluorine atom is attached on one side of the layer, then fluorine is attached on the opposite side of the layer for the adjacent carbon atoms. For fluorographene layers of other types, fluorine atoms attached to one side of the layer form various clusters. For T2 and T3 layer types fluorine atoms form islands of two atoms. In T4 and T5 layer types the islands contain four and eight atoms, respectively, and in the T6 layer, fluorine atoms attached to one side of the graphene layer form a ribbon with a chair structure.

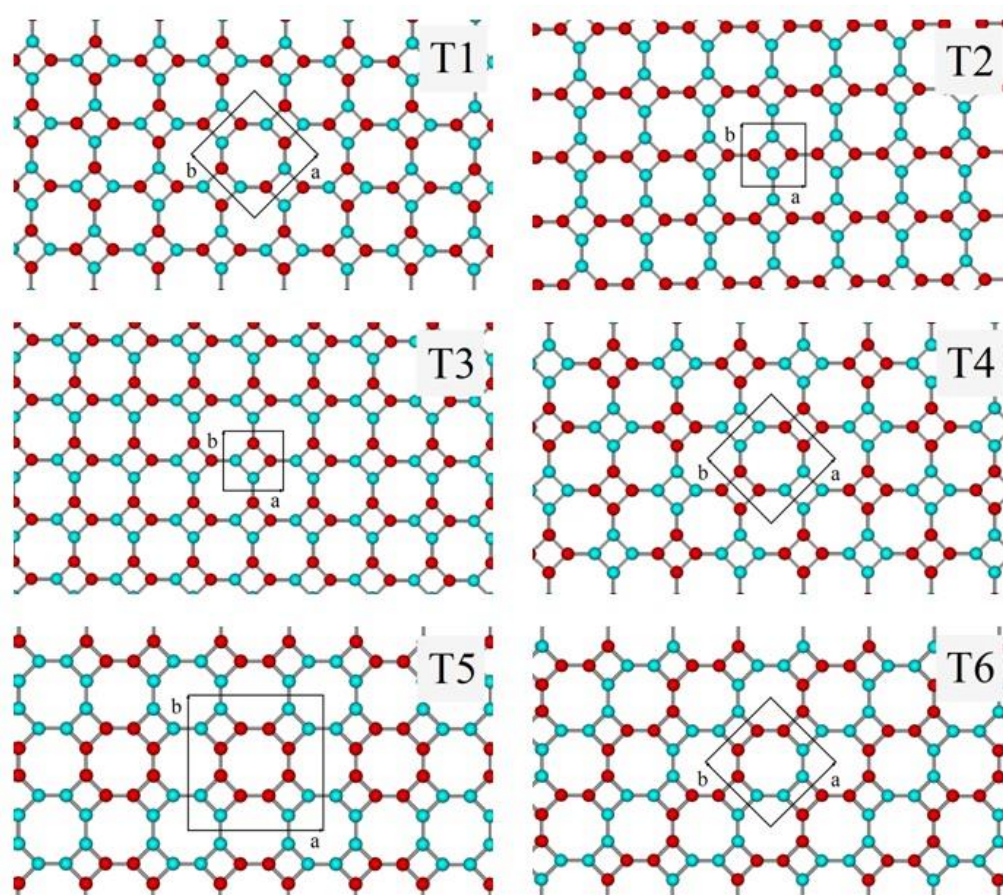


Figure 1. Possible types (T1-T6) of the attachment of non-carbon atoms to the graphene L_{4-8} layer (different colors highlight carbon atoms to which non-carbon atoms are attached on opposite sides of the layer, the elementary square cells with elementary translations vectors $a = b$).

Calculations of geometrically optimized structure and electronic properties of model-built layers of T1-T6 fluorographene types were performed using the density functional theory (DFT) method. In the simulation, a generalized gradient approximation (GGA) was used. The calculations were performed for three-dimensional crystals consisting of fluorographene layers, the distance between which was 12 Å. The interlayer distance was chosen so that the neighboring layers did not interact with each other, and

the optimal structure and properties of the individual isolated layers were obtained in the calculations. The simulation used a gradient approximation and a grid of 12x12x12 k-points.

3. Results

Geometrically optimized structure of the fluorographene layers formed during fluorination of the graphene layer L₄₋₈, calculated using the DFT-GGA method, is shown in figure 2. As a result, the layers were corrugated, so that the fluorine atoms displaced the carbon atoms from the initial position in the direction of the plane. Structure of the T3 type layer collapsed during the geometrical optimization. The structure of this layer, shown in figure 2, structural characteristics and properties shown in table 1 and given for the last stage of calculations after which destruction of the structure begins.

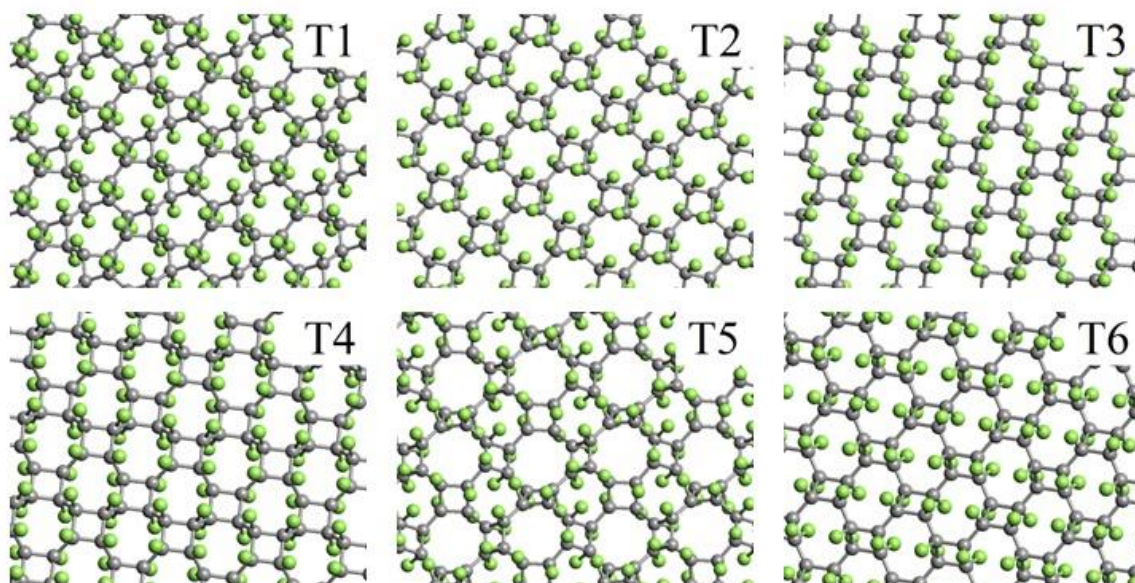


Figure 2. Geometrically optimized structure of T1-T6 polymorphic varieties of the fluorographene layer L₄₋₈.

Table 1. Structural parameters and properties of polymorphic varieties of the fluorographene layer L₄₋₈.

Parameters	CF-L ₄₋₈ layers					
	T1	T2	T3	T4	T5	T6
Crystal family	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Orthorhombic
Translation vector <i>a</i> (Å)	5.0674	3.6607	3.5002	4.8759	7.0879	4.8955
Translation vector <i>b</i> (Å)	5.0674	3.6607	3.5002	4.8759	7.0879	4.8753
Number of atoms in the unit cell	16	8	8	16	32	16
Layer density (mg m ⁻²)	1.5581	1.4929	1.6329	1.6830	1.5928	1.6764
Total energy (eV (CF) ⁻¹)	-800.30	-799.68	-800.41	800.37	799.88	800.33
Sublimation energy (eV (CF) ⁻¹)	13.98	13.36	14.09	14.05	13.56	14.01
Fermi energy (eV)	-6.042	-6.019	-5.914	-6.305	-5.889	-5.943
Band gap (eV)	3.2105	4.9582	3.0516	3.9464	4.6864	4.8774

The crystal lattices of T1 - T5 types of fluorographene layers belong to the tetragonal crystal family, and for the T6 layer - to the orthorhombic one. The unit cells of CF-L₄₋₈ layers contain from 8 atoms (for the T2 and T3 layers) to 32 atoms (with a T5 type layer). The calculated values of the elementary translation vectors vary from 3.5002 Å (T3 layer) to 7.0879 Å (T5 layer) (table 1). The lowest layer

density (1.4929 mg m^{-2}) is observed for the fluorographene layer of the T2 type, the highest (1.6830 mg m^{-2}) is observed for the T5 type layer.

The sublimation energy of the fluorographene layers varies in the range from 13.36 to 14.09 eV/(CF). Moreover, the maximum value of the sublimation energy is observed for CF- L_{4-8} layer of T3 type, which collapsed during optimization. Thus, the sublimation energy is not a parameter that uniquely characterizes the stability of the structure of the fluorographene layers.

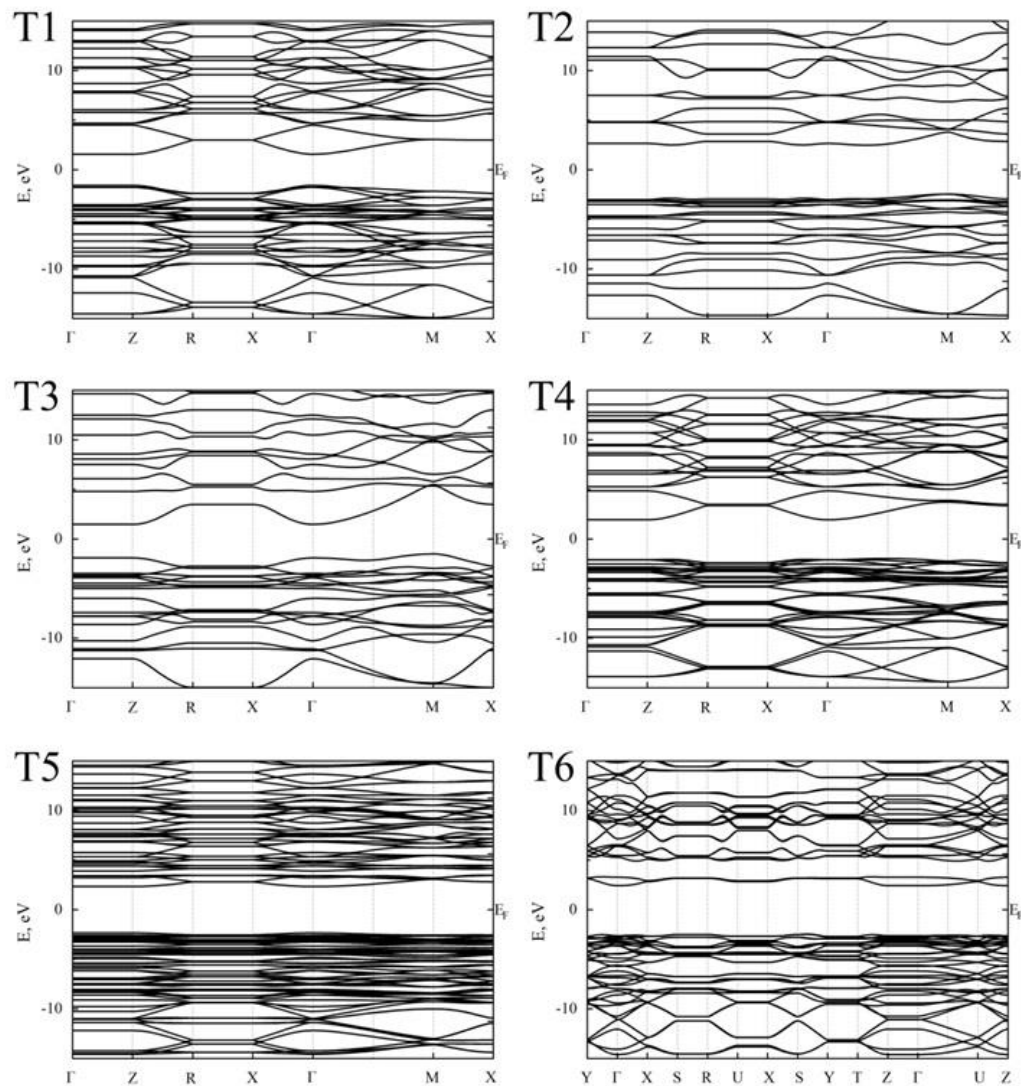


Figure 3. The band structure of the T1-T6 polymorphic varieties of the fluorographene layer L_{4-8} (the Fermi energy E_F is taken as the origin on the energy axis).

The band gap of the CF- L_{4-8} fluorographene layers was determined by calculating the band structure and the density of electronic states. Figure 3 shows the diagrams of the band structure, and table 1 shows the calculated values of widths of the band gaps. The minimum band gap (3.0516 eV) is observed for the CF- L_{4-8} layer of the third type, and the maximum (4.9582 eV) is observed for the layer of the second type. The range of changes in the electronic characteristics of polymorphic varieties of fluorographene formed on the basis of L_{4-8} graphene layer is larger than the similar range for polymorphs of fluorographene on the basis of L_6 graphene [12]. New polymorphic varieties of fluorographene can be used to design nanoelectronic devices.

Acknowledgments

This work was supported by Foundation for perspective scientific research of Chelyabinsk State University.

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