New polymorphic varieties of fluorographene forming during fluorine functionalization of 4-8 graphene layers

Maxim E Belenkov¹, Vladimir M Chernov¹ and Evgeny A Belenkov¹
¹Department of Physics, Chelyabinsk State University, Chelyabinsk 454001, Russia
E-mail: me.belenkov@gmail.com

Abstract. Using the methods of the density functional theory in the generalized gradient approximation, the structure and electronic properties of six new polymorphic varieties of fluorographene, formed during the chemical adsorption of fluorine by a 4-8 graphene layer, are calculated. The sublimation energy of 4-8 polymorphs of fluorographene varies from 13.36 to 14.09 eV (CF)⁻¹. The range of variation of the band gap of new CF-L₄₋₈ polymorphs of fluorographene is greater than the similar interval for CF-L₆ compounds.

1. Introduction
It is possible to modify the properties of graphene from metallic to semiconductor due to chemical adsorption of hydrogen, fluorine, chlorine, oxygen and other atoms on its surface [1-4]. The most promising is the functionalization of graphene by fluorine, since the fluorographene compounds are more thermally stable than others. It is possible to obtain various structural modifications of fluorinated graphene differing by the order of addition of fluorine atoms [5-7]. These polymorphic varieties may have different electronic properties, but their variation intervals are rather narrow. It is possible to obtain new structural varieties of fluorographene with a large range of changes in properties by chemically adsorbing fluorine on the surface of various polymorphs of graphene [8]. In this work, we studied compounds of fluorographene with a layered structure that can be obtained by fluorination of 4-8 graphene layers.

2. Methods
Theoretical analysis of possible ways of chemical adsorption on the surface of L₄₋₈ graphene layers showed that there are six main possible polymorphic varieties of fluorographene, differing by the order of attachment of fluorine atoms to the graphene layer. Calculations of the geometrically optimized structure of CF-L₄₋₈ layers and their electronic properties were performed by the density functional theory (DFT) method in the generalized gradient approximation (GGA). Calculations were carried out for bulk structures – stacks of fluorographene layers with a spacing of 12 Å between the layers. This distance ensured the absence of influence of adjacent layers on each other. The calculations used a set of k-points: 12 × 12 × 12. The dimension of the set of basis functions was limited by the value E_cutoff = 1 keV.

3. Results
During the geometrical optimization of the structure of six theoretically constructed varieties of CF-L₄₋₈ fluorographene, five layers (structural types T1, T2, T4-T6) turned out to be stable, and one
layer (structural type T3) collapsed after breaking up into separate atoms. The geometrically optimized structure of the layers and their unit cells are shown in figure 1. For a layer of T3 type, the structure is shown after partial optimization, before the start of fracture. The crystal lattices of the fluorographene layers of the T1-T5 types are tetragonal, and the T6 layer has a rhombic type (table 1). The unit cells of the layers contain from 8 to 32 atoms. The lengths of the elementary translations vectors for crystal lattices of different types are given in table 1. The layer density of the polymorphs of the fluorographene varies from the minimum value of 1.558 mg m$^{-2}$ (T1 layer type) to the maximum value 1.683 mg m$^{-2}$ (T4 layer type).

The results of measurements of the lengths of interatomic bonds are given in table 2. The first bond having the length $L_1$ is the bond between the fluorine and the carbon atoms. The length of this bond varies from 1.4196 to 1.4869 Å. In the T1-T4 layers and the T6 layer, all carbon atoms are in equivalent structural positions and, therefore, the lengths of the CF bonds are the same for each layer. In the T5 type layer, there are two different structural positions of atoms and, therefore, the length of CF bonds is different (table 2). The second carbon-carbon bond having a length $L_2$ is located between adjacent octagons of $L_{4,8}$ layers. This bond is shorter than the carbon-carbon bond lengths of $L_3$ and $L_4$, which are sides of quadrangles. The lengths of the $L_3$ and $L_4$ bonds in each of the layers have close values, i.e. the shape of the quadrilateral is close to square. For the T3 type layer, which was not stable, the $L_4$ bond length is minimal compared to other layers and a significant difference from $L_3$. This may cause instability of the structure of the T3 type layer. For carbon-carbon bonds, table 2 also

![Figure 1](image_url)

**Figure 1.** The unit cells and the geometrically optimized structure of polymorphic varieties of fluorographene layers based on the graphene layer $L_{4,8}$: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5; (f) T6.
shows the mutual orientation of fluorine atoms at the ends of the corresponding bond. Only in the T1 type layer for each of the three carbon-carbon bonds is the orientation opposite.

Table 1. Structural parameters and properties of polymorphic varieties of the fluorographene layer L_{4-8} (a, b – translation vectors, N – number of atoms in the unit cell, \( \rho \) – layer density, \( E_{\text{total}} \) – total energy, \( E_{\text{sub}} \) – sublimation energy, \( E_{F} \) – Fermi energy, \( \Delta \) – band gap).

| Crystal family | Type | T1 | T2 | T3 | T4 | T5 | T6 |
|----------------|------|----|----|----|----|----|----|
| a (Å)          | Tetragonal | 5.0674 | 3.6607 | 3.5002 | 4.8759 | 7.0879 | 4.8955 |
| b (Å)          | Tetragonal | 1.558 | 1.493 | 1.633 | 1.683 | 1.593 | 1.676 |
| N (atom)       | Tetragonal | 16 | 8 | 8 | 16 | 32 | 16 |
| \( \rho \) (mg m\(^{-2}\)) | Tetragonal | -800.30 | -799.68 | -800.41 | 800.37 | 799.88 | 800.33 |
| \( E_{\text{sub}} \) (eV (CF\(^{3}\)) | Tetragonal | 13.98 | 13.36 | 14.09 | 14.05 | 13.56 | 14.01 |
| \( E_{F} \) (eV) | Tetragonal | -6.042 | -6.019 | -5.914 | -6.305 | -5.889 | -5.943 |
| \( \Delta \) (eV) | Tetragonal | 3.2105 | 4.9582 | 3.0516 | 3.9464 | 4.6864 | 4.8774 |

Table 2. The lengths of interatomic bonds (\( L_{i} \)) for fluorographene L_{4-8} layers of various types.

| Type | L_{1}, Å | L_{2}, Å | L_{3}, Å | L_{4}, Å |
|------|-----------|-----------|-----------|-----------|
| T1   | 1.4400    | 1.5064    | ↑↓         | ↑↓         | 1.6081    | ↑↓         |
| T2   | 1.4869    | 1.5388    | ↑↑         | ↑↑         | 1.6032    | ↑↑         |
| T3   | 1.4204    | 1.5246    | ↑↓         | ↑↑         | 1.6089    | ↑↑         | 1.5737 |
| T4   | 1.4196    | 1.5343    | ↑↑         | ↑↑         | 1.6083    | ↑↑         | 1.6082 |
| T5   | 1.4747    | 1.5888    | ↑↑         | ↑↑         | 1.6126    | ↑↑         | 1.6028 |
| T6   | 1.4209    | 1.5888    | ↑↑         | ↑↑         | 1.6268    | ↑↑         | 1.6028 |

The values of the angles between the interatomic bonds in the structure of the L_{4-8} fluorographene layers are given in table 3. The values of the angles vary in the interval from 83.80 to 134.59 °. The atoms in the structure of the fluorographene layers are in sp\(^{3}\) hybridized states and the equilibrium value of the angles between the bonds should be 109.47 °. This value is characteristic for interatomic bonds in the diamond structure. To estimate the degree of deformation of the structure of graphene layers compared to the equilibrium structure, the values of the deformation parameter Def were calculated. This parameter was found as the sum of the absolute values of the difference in the angles between the bonds in the layer and the angle between the bonds in the diamond. The values of the parameter Def are given in table 3. The minimum value of Def equal to 48.54 ° is observed for the T3 layer, and the maximum value is 113.03 ° for the layer of the T2 type.

Table 3. Angles (\( \phi_{ij} \)) between interatomic bonds and deformation parameters (Def) for fluorographene L_{4-8} layers of various types.

| Type | \( \phi_{12}, \) ° | \( \phi_{13}, \) ° | \( \phi_{14}, \) ° | \( \phi_{23}, \) ° | \( \phi_{24}, \) ° | \( \phi_{34}, \) ° | Def, ° |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------|
| T1   | 103.28          | 110.92          | 110.92          | 123.11          | 123.11          | 84.94           | 60.9   |
| T2   | 98.39           | 89.59           | 121.47          | 142.35          | 120.99          | 83.80           | 113.03 |
| T3   | 106.36          | 107.41          | 112.07          | 124.62          | 115.62          | 90.00           | 48.54  |
| T4   | 107.28          | 105.97          | 105.97          | 122.73          | 122.73          | 90.00           | 55.18  |
| T5   | 100.55          | 91.24           | 96.67           | 134.03          | 127.99          | 93.78           | 98.72  |
| T6   | 101.69          | 101.84          | 124.60          | 134.59          | 110.29          | 86.23           | 79.72  |
The calculated sublimation energies of the CF-L$_{4-8}$ layers with a stable structure are in the range from 13.36 to 14.09 eV (CF)$^{-1}$. The dependence of the sublimation energy of the fluorographene layers on the values of the deformation parameters characterizing their structure is observed – the greater the value of the deformation parameter, the lower the sublimation energy (figure 2).

As a result of the DFT-GGA calculations, the band structures and densities of electronic states of L$_{4-8}$ fluorographene polymorphs were found (figure 3, 4). All the investigated layers of fluorographene turned out to be semiconductors with a band gap from 3.21 eV for the T1 layer to 4.96 eV for the T2 layer. The range of variation of the band gap in polymorphic varieties of L$_{4-8}$ layers of fluorographene turned out to be longer than the same interval for L$_6$ fluorographene layers [6]. New structural types of fluorographene, theoretically investigated in this paper, can find practical application in the design of nanoelectronic devices.

**Figure 2.** The dependence of the sublimation energy ($E_{sub}$) on the deformation parameter (Def) for polymorphic varieties of L$_{4-8}$ layers of fluorographene.

**Figure 3.** The density of electronic states (DOS) of polymorphic varieties of fluorographene layers based on the graphene layer L$_{4-8}$: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5; (f) T6.
Figure 4. The band structure of polymorphic varieties of fluorographene layers based on the graphene layer L4,8: (a) T1; (b) T2; (c) T3; (d) T4; (e) T5; (f) T6.

Acknowledgments
This research was supported by Foundation for Perspective Scientific Research of Chelyabinsk State University.

References
[1] Elias D C, Nair R R, Mohiuddin T M G, Morozov S V, Blake P, Halsall M P, Ferrari A C, Boukhvalov D W, Katsnelson M I, Geim A K and Novoselov K S 2009 Science 323 610
[2] Robinson J T, Burgess J S, Junkermeier C E, Badescu S C, Reinecke T L, Perkins F K, Zalalutdniov M K, Baldwin J W, Culbertson J C, Sheehan P E and Snow E S 2010 Nano Letters 10 3001
[3] Li B, Zhou L, Wu D, Peng H, Yan K, Zhou Y and Liu Z 2011 ACS Nano 5 5957
[4] Chen D, Feng H and Li J 2012 Chem. Rev. 112 6027
[5] Belenkov M E, Chernov V M and Belenkov E A 2018 Materials research proceedings 9 148
[6] Belenkov M E, Chernov V M and Belenkov E A 2018 IOP J. Phys. Conf. Ser. 1124 022010
[7] Grishakov K S, Katin K P, Maslov M M and Prudkovskiy V S 2019 Appl. Surf. Sci. 463 1051
[8] Belenkov E A and Kochengin A E 2015 Phys. Solid State 57 2126