Computer simulation of crystals formed from 4-6-12 and 5-7 fluorographene layers

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Abstract. The three-dimensional structure of four fluorographene crystals was calculated by the atom-atom potential method. The crystals consisted of 4-6-12 or 5-7 graphene layers functionalized by fluorine packed in stacks. The structure of fluorographene layers of two polymorphs T1 and T3 for 4-6-12 layer and two polymorphs of 5-7 layer T1 and T2 was considered. The electronic structure was calculated by the density functional theory method in the generalized gradient approximation. As a result of the calculations, it was established that the interlayer distances in various fluorographene crystals vary in the range from 5.4921 to 5.7645 Å. In CF-L4-6-12 T1 crystals, the relative shift of adjacent layers is close to zero. In the remaining fluorographene crystals, the layer shift vector varies from 0.336 to 0.3714 nm. The energy of interlayer bonds per atom is minimal for CF-L5-7 crystal of T2 type and is -3024.44 J/mol. The maximum value of the binding energy is equal to -2291.35 J/mol and observed in CF-L4-6-12 crystals of T3 type. The sublimation energy varies from 13.83 to 14.24 eV, and the band gap varies from 2.827 to 3.682 eV. The band gap in CF crystals is 0.2–0.4 eV less than in isolated fluorographene layers.

1. Introduction
The functionalization of graphene by attaching non-carbon atoms to it makes it possible to change its electronic properties [1]. Graphene can be functionalized by hydrogen, oxygen, chlorine, fluorine and other atoms or molecular groups [2-7]. Of the various compounds of functionalized graphene, fluorographene seems to be the most promising, since it has the greatest stability [5-7]. The possibility of the existence of various fluorinated graphene polymorphic varieties, which differ in the order of chemical adsorption of fluorine atoms on graphene layers, has been established theoretically [8-13]. Due to this, it is possible to form a number of structural varieties with properties that vary in wide ranges. It is possible to form five main polymorphic varieties on the basis of hexagonal graphene [8, 9]. In addition, a number of fluorographene polymorphs can be formed by fluorination of other structural varieties of graphene, such as L4-8, L3-12, L4-6-12, or L5-7 [10-13]. The structure and properties of these functionalized graphene compounds have been theoretically investigated for isolated layers. However, in nature, layers of graphene and functionalized graphene exist in the form of crystals, in which individual layers are packed in stacks. The properties of three-dimensional crystals differ from the properties of monolayers. For example, in the monolayers of graphene, the band gap width is zero [14], and in graphite crystals, there is an overlap of the valence band and the conduction band in a region about 0.04 eV wide [15]. Therefore, for the correct prediction of the properties of fluorographene crystals, calculations performed specifically for crystals, and not for monolayers, are
necessary. In this paper, computer simulation was carried out for fluorographene crystals formed from the CF-L_{4.6-12} or CF-L_{5.7} layers.

2. Computer simulation methods

In fluorographene crystals, the structure of an individual layer is formed by covalent bonds between carbon and fluorine atoms. The interaction between the fluorographene layers is carried out by Van der Waals bonds. Ab initio methods are good fit to simulate the structure and properties of the compounds with covalent chemical bond type. Therefore, the method of density functional theory in the generalized gradient approximation was used to calculate the structure of individual layers. The structure of compounds with Van der Waals bonds is more correctly modeled by molecular mechanics methods. Therefore, the atom-atom potential method was used to calculate the three-dimensional structure of fluorographene crystals [16].

Four different polymorphic varieties of fluorographene layers - CF-L_{4.6-12} T1 and T3 types, as well as CF-L_{5.7} T1 and T2 were used to construct fluorographene crystals. It is these polymorphic varieties of fluorinated graphene that are stable. The initial structure of the layers is shown in figure 1 and was obtained as a result of the calculations described in [12, 13]. The unit cells of these layers were chosen to be rectangular. For 4-6-12 layers, the unit cells contained 48 CF molecular groups, and for 5-7 layers – 32 CF molecular groups (figure 1, table 1).

![Figure 1](image1.png)

**Figure 1.** Images of the structure of fluorographene layers and their elementary cells: (a) CF-L_{4.6-12} of the T1 type; (b) CF-L_{4.6-12} of the T3 type; (c) CF-L_{5.7} of the T1 type; (d) CF-L_{5.7} of the T2 type.
The parameters of the structure and some properties of CF-L_{4.6-12} and CF-L_{5.7} fluorographene crystals.

| The type of the structure | CF-L_{4.6-12} T1 | CF-L_{4.6-12} T3 | CF-L_{5.7} T1 | CF-L_{5.7} T2 |
|--------------------------|------------------|------------------|---------------|---------------|
| N_{UC} (atom)            | 96               | 96               | 64            | 64            |
| a (Å)                    | 7.080            | 6.854            | 6.004         | 5.902         |
| b (Å)                    | 12.263           | 11.871           | 7.783         | 7.572         |
| c (Å)                    | 10.984           | 11.529           | 11.000        | 11.112        |
| N_{L} (atom)             | 17310            | 18528            | 5385          | 5615          |
| d_{0} (Å)                | 5.493            | 6.098            | 5.555         | 5.996         |
| ΔX (nm)                  | 0.0001           | 0.2140           | 0.3664        | 0.2632        |
| ΔY (nm)                  | 0.0052           | 0.2716           | 0.0606        | 0.2092        |
| S (nm)                   | 0.0052           | 0.3458           | 0.3714        | 0.3362        |
| d_{S} (Å)                | 5.4921           | 5.7645           | 5.4999        | 5.5558        |
| E_{VdW} (J mol^{-1})     | -2299.43         | -2291.35         | -2802.17      | -3024.44      |
| ρ (g cm^{-3})            | 2.592            | 2.635            | 3.206         | 3.318         |
| E_{total} (eV (u.c.))    | -38410.6         | -38407.8         | -25607.5      | -25617.6      |
| E_{total} (eV (CF))      | -800.22          | -800.16          | -800.23       | -800.55       |
| E_{sub} (eV (CF))        | 13.89            | 13.83            | 13.90         | 14.24         |
| E_{sub} (eV (CF))        | 13.84^a          | 13.80^a          | 13.85^b       | 14.17^b       |
| Δ (eV)                   | 2.827            | 3.682            | 3.663         | 3.126         |
| Δ_{s} (eV)               | 3.193^a          | 4.150^a          | 4.09^b        | 3.32^b        |
| E_{F} (eV)               | -5.243           | -4.985           | -5.196        | -5.159        |

N_{UC} – the number of atoms in a unit cell; a, b, c – the vectors of translations; N_{L} – the number of atoms in the fragments of layers in calculations by the atom-atom potential method; d_{0}, d_{S} – interlayer distances at zero and optimal shift vectors; S – the shift vector at which the minimum energy of interlayer bonds is observed; ΔX, ΔY – the components of the shift vector S; E_{VdW} is the specific energy of interlayer Van der Waals bonds per one CF molecular group; ρ – the density of fluorographene crystals; R – the average value of the interatomic bond lengths; E_{total} – the total energy per unit cell or CF molecular group; E_{sub} – the sublimation energy; Δ – the band gap at the Fermi energy level (E_{F}).

^a The parameter values calculated in [12] for isolated CF-L_{4.6-12} fluorographene monolayers.

^b The parameter values calculated in [13] for isolated CF-L_{5.7} fluorographene monolayers.

For calculations by the atom-atom potential method based on a set of empirical data [17], constants were selected for three interatomic potentials: C-C, C-F, and F-F. Fluorographene crystals were considered as a stack of layers of fluorinated graphene arranged parallel to each other (Fig. 2 a). The total energy (E_{VdW}) of interlayer bonds in crystals was calculated at various relative positions of neighboring layers. As a result of these calculations, the structure corresponding to the minimum binding energy was found. The relative position of adjacent layers was determined by two parameters: the interlayer distance (d_{0}) and the layer shift vector (S) (Fig. 2). The calculations were performed using a specially written program on C++ programming language.

The electronic structure of CF crystals was calculated by the density functional theory (DFT) method [18] in the generalized gradient approximation (GGA) [19]. The calculations were performed using the Quantum ESPRESSO software package [20]. The initial structures for these calculations were the structures found as a result of modeling by the atom-atom potential method.

3. Results and discussion

The calculations by the atom-atomic potential method have shown that the distance d_{0} between adjacent layers in CF crystals at zero relative shift varies in the range from 5.493 to 6.098 Å (table 1). At constant values of interlayer distances d_{0}, relative shifts of neighboring layers were performed. The values of the shift vectors were set by the components ΔX and ΔY of the vector S. The components of the vector changed in increments of 1/20 from the values of the vectors of translations a and b. Therefore, the energy of interlayer bonds was calculated at 441 different values of the shift vector S.
Based on the results of the calculations, graphs of the interlayer bond energy versus the shift vector were constructed, shown in figure 3. The analysis of the calculated data made it possible to find the values of the shift vector corresponding to the minimum energy of interlayer bonds (table 1). With the values of the shift vector found, calculations of the interlayer distances \( d_S \) (table 1) corresponding to the minimum binding energy were performed, as a result of which the optimal crystal structure was found.

![Figure 2](image.png)

**Figure 2.** Scheme for setting the interlayer distances \( d_S \) (a) and the relative shift of the layers set by the vector \( S \) (b) using the CF-L_{4-6-12} crystal of the T3 type as an example.

The energy of interlayer bonds per atom is minimal for a CF-L_{5-7} crystal of the T2 type and is \(-3024.44 \text{ J/mol}\). The maximum binding energy value of \(-2291.35 \text{ J/mol}\) is observed in CF-L_{4-6-12} crystals of the T3 type. The density of fluorographene crystals varies in the range of \(2.592 - 3.318 \text{ g/cm}^3\). The sublimation energy calculated from the results of DFT-GGA calculations is minimal for a CF-L_{4-6-12} crystal of the T3 type \((13.83 \text{ eV})\), the maximum value is observed for a CF-L_{5-7} crystal of the T2 type \((14.24 \text{ eV})\).

The sublimation energy of fluorographene layers varies in the range from \(13.83\) to \(14.24 \text{ eV/(CF)}\), which is \(0.03 - 0.07 \text{ eV/(CF)}\) less than for isolated monolayers (table 1). The band gap at the Fermi energy level in the band structure of CF crystals varies from \(2.827\) to \(3.682 \text{ eV}\). The values of the band gap widths in fluorographene crystals are \(0.2 \div 0.4 \text{ eV}\) less than the value of this parameter for the corresponding isolated layers of fluorinated graphene.

### 4. Summary

The three-dimensional structure of four polymorphic varieties of fluorographene crystals: CF-L_{4-6-12} of the T1 and T3 types, as well as CF-L_{5-7} of the T1 and T2 types, was calculated by the atom-atom potential method. As a result of calculations, it was established that the optimal crystal structure corresponds to fluorographene layers located at distances from \(5.4921\) to \(5.7645 \text{ Å}\) and shift vectors varying from \(0.0052\) to \(0.3714 \text{ nm}\). The density of fluorographene crystals varies from \(2.592\) to \(3.318 \text{ g/cm}^3\). DFT-GGA calculations showed that all 4 fluorographene crystal types must be semiconductors. The band gap is minimal for CF-L_{4-6-12} crystal of the T1 type and is equal \(2.827 \text{ eV}\), maximal for CF-L_{4-6-12} crystal of the T3 type and is \(3.682 \text{ eV}\). The band gap in three-dimensional crystals is less than the band gap for the corresponding isolated monolayers of fluorinated 4-6-12 and 5-7 graphene [12, 13]. The new fluorographene polymorphs studied within this work can find practical application in electronics [21-23].
Figure 3. Dependence of the specific energy of interlayer bonds (E) on the relative shift vector of layers S (ΔX, ΔY) in fluorographene crystals: (a) CF-L₄₋₆₋₁₂ of the T₁ type; (b) CF-L₄₋₆₋₁₂ of the T₃ type; (c) CF-L₅₋₇ of the T₁ type; (d) CF-L₅₋₇ of the T₂ type.

5. References
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