
«Calculations of the three-dimensional crystal structures consisting of 4-8 graphene layers functionalized with fluorine»

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Polymorphs of graphene and functionalized graphene make it possible to change the electronic properties, which is important for practical applications. The structure and properties of such compounds are usually calculated for isolated monolayers. However, in nature, graphene layers exist packed in three-dimensional graphite crystals and their properties change because of this. Earlier, in a number of works, new polymorphic varieties of fluorographene, formed on the basis of 4-8 graphene, were theoretically predicted. The structure and properties of these compounds were obtained as a result of theoretical calculations of individual monolayers. In this paper, the calculations of the three-dimensional structure of crystals are performed, which are formed from layers of 4-8 graphene functionalized with fluorine as a result of their parallel packing into crystals.
The structures previously calculated by first-principle methods for isolated layers of 4-8 graphene functionalized with fluorine were taken as the initial structure of the layers (Fig. 1). In total, the existence of six polymorphs of 4-8 fluorographene is theoretically possible, but one of these structural varieties of the T3 type is unstable. Therefore, the study was performed for five stable polymorphic varieties of 4-8 fluorographene of T1, T2, T4, T5 and T6 structural types. When calculating the structure of CF-L4-8 crystals, rectangular unit cells containing from 8 to 32 atoms were chosen as the unit cells of fluorographene layers of the T1, T2, T4-T6 structural types. The atom-atomic potential method was used to calculate the interlayer interactions in fluorographene crystals. For these calculations, a program was written in the C++ language. The electronic structure of fluorographene crystals was calculated in the Quantum ESPRESSO software package using the density functional theory (DFT) method in the generalized gradient approximation (GGA).
Figure 1. Elementary cells of polymorphic varieties of the CF-L₄₈ layers selected for modeling of the three-dimensional structure of crystals: (a) T1 – type; (b) T2 – type; (c) T4 – type; (d) T5 – type; (e) T6 – type; (f) the scheme for specifying the relative position of adjacent fluorographene layers in the T5 type crystals when modeling a three-dimensional structure.
Table 1. The structural parameters and some properties of CF-L₄₋₈ fluorographene crystals (Nₑₑₑ – the number of atoms in a unit cell; a, b, c – vectors of elementary translations; Nₜₜ – the number of atoms in fragments of layers in calculations by the method of atom-atom potential; dₒ, dₛ – interlayer distances at zero and the optimal shift vectors; S – shift vector at which the minimum energy of interlayer bonds is observed; ΔX, ΔY – components of the shift vector S; $E_{vdw}$ – the binding 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; $E_{total}$ – total energy per unit cell or CF molecular group; $E_{sub}$ – the sublimation energy; Δ – the band gap at the Fermi energy level ($E_F$); * – the parameter values calculated in papers [9, 21] for isolated monolayers of fluorographene).

<table>
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<tr>
<th>Structure type</th>
<th>T1</th>
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<th>T4</th>
<th>T5</th>
<th>T6</th>
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Figure 2. The energy of interlayer bonds ($E$) versus the vector of the relative shift of the layers $S$ ($\Delta X, \Delta Y$) in CF-L$_{13}$ fluorographene crystals: (a) T1 - type; (b) T2 - type (c) T4 - type; (d) T5 - type; (e) T6 - type.
Figure 3. Band structure and density of electronic states (DOS) of polymorphic varieties of the CF-L_{4−8} layers selected for modeling of the three-dimensional structure of crystals: (a) T1 – type; (b) T2 – type; (c) T4 – type; (d) T5 – type; (e) T6 – type.
Conclusions

Thus, the calculations of the three-dimensional structure of T1, T2, T4-T6 polymorphic varieties of 4-8 crystals of fluorographene were performed by the method of atom-atomic potential. As a result of calculations, it was found that the minimum interlayer bond energies are observed at interlayer distances varying from 5.183 to 5.959 Å and shift vectors varying from 0 to 0.3138 nm. The density of fluorographene crystals is $2.752 \div 3.124$ g/cm$^3$. When calculating the electronic structure of fluorographene crystals by the DFT-GGA method, it was established that all of them should exhibit semiconducting properties. The band gap for crystals varies in the range from 2.7806 to 4.5988 eV. The band gap in three-dimensional crystals is $0.359 \div 0.620$ eV less than the band gap for the corresponding isolated monolayers of fluorinated 4–8 graphene [9, 21]. New polymorphs of fluorinated 4-8 graphene can be used in nanoelectronics to create high-performance electronic computing systems [1-4].

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