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# First-Principles Calculation of Electronic Properties of Fluorinated Graphene

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**Abstract.** We have studied structural and electronic properties of fluorinated graphene with different coverage of fluorine using first-principles calculations based on the density functional theory. The atomic structures and electronic structures of fluorinated graphene are investigated. Our results show that the electronic properties of a fluorinated graphene sheet exhibit strong dependence on the degree of fluorination. Our study suggests that the property of graphene can be modified by absorbing different amounts of fluorine.

## INTRODUCTION

Graphene is a single atomic layer of graphite, which exhibits the exceptional structural, mechanical, electrical and optical properties. These properties of graphene make it a promising material for a wide range of applications in flexible electronics, nanoelectronics, energy conversion and storage devices [1, 2, 3, 4]. The absence of a band gap in graphene limits its application in various nanoelectronics devices.

Chemical modification of graphene layers is of great importance for development of new materials, since it not only opens the band gap, but also makes it possible to control its width. Therefore, one of the research areas of such systems is chemical functionalization. Graphene fluorides attract interest from the point of view of obtaining heterostructures with the controlled band gap, which can be of great importance for the production of photodetectors or storage devices. Fluorinated graphene has been experimentally obtained for various fluorine coverage and distribution [5, 6, 7, 8]. The structural, mechanical and electronic properties of fluorinated graphene have been investigated both experimentally and theoretically [8, 9, 10, 11, 12, 13, 14]. It became possible to control the width of the band gap by a controlled change in the density of fluorination. Experimental studies of selective fluorination of graphene layers by removal of fluorine atoms from graphene using an electron beam [7] or local deposition of a fluorine atom by laser irradiation with fluoropolymers are carried out [8].

In the present work, we investigate the atomic structure of partially fluorinated graphene with different concentrations of fluorine atoms on its surface and study the change in its electronic properties as a function of the concentration and mutual arrangement of adsorbed atoms on the surface.

## METHODOLOGY

All calculations are performed within the framework of the density functional theory (DFT), using the pseudopotential method in the basis of plane waves, implemented in the Quantum Espresso code (software package) [15]. The generalized gradient approximation (GGA) exchange-correlation functional in the Perdew-Burke-Ernzerhof (PBE) form is adopted in the structural optimization and electronic structure calculations of different concentrations of fluorine atoms. An electron-ion interaction was taken into account using an ultra soft pseudopotential for the carbon and fluorine atoms Rappe-Rabe Kaxiras-Joannopoulos (RRKJ). The basis functions were plane waves with a cutoff energy  $E_{cut} = 540$  eV. Sampling of the Brillouin zone is performed using the  $k$ -point mesh generated by the Monkhorst-Pack scheme [16]. Converged  $k$ -point grids corresponding to a  $16 \times 16 \times 1$  grid for a graphene unit cell are used for different graphene supercells. For all systems, relaxation of basis vectors and atomic coordinates are performed

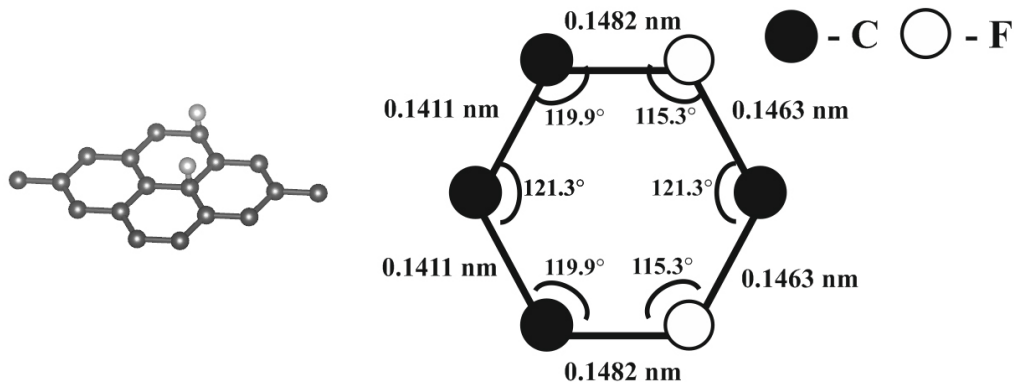
by minimizing the total energy. The structural optimization has been conducted using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization until residual forces on the atoms are lower than  $10^{-4}$  eV/Å. To avoid the interaction between layers of the adjacent fluorinated graphene sheets, a vacuum space of 15 Å in the  $z$  direction perpendicular to the atomic plane is used in the supercell. In this paper, we investigate the fluorinated graphene at the different concentrations of fluorine atoms  $CH_x$ , where  $x = n_F/n_C$ ,  $n_F$  is the number of fluorine atoms, and  $n_C$  is the number of carbon atoms. The value of  $x$  will characterize the degree of graphene adsorption of fluorine atoms. To model the properties of the  $CH_x$  structure, we use the supercells, whose dimensions are given in Table 1.

**TABLE 1.** Supercell Size Chosen in Calculations of Fluorinated Graphene Sheets

$CH_x$	$x = n_F/n_C$	Supercell Size
$CH_{0.111}$	2/18	$3 \times 3$
$CH_{0.125}$	1/18	$3 \times 3$
$CH_{0.167}$	3/18	$3 \times 3$
$CH_{0.222}$	4/18	$3 \times 3$
$CH_{0.25}$	2/8	$2 \times 2$

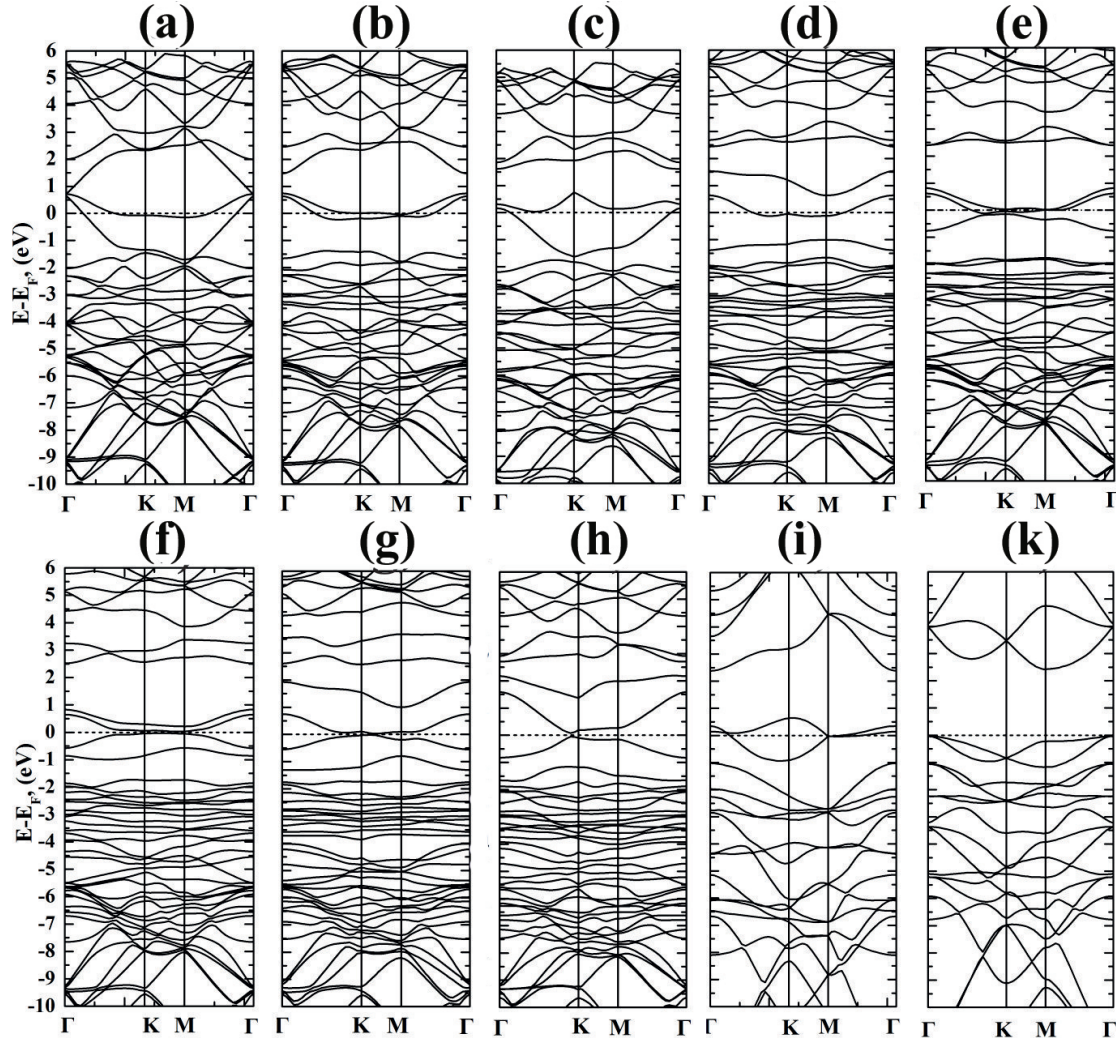
## RESULTS AND DISCUSSION

The unit cell of graphene has two carbon atoms, which defined the A and B sublattices. When only a single F atom is considered for the given supercell, all the F atoms are bonded with C atoms belonging to the same sublattice. The system is called  $CF_x^{AA}$ . The effect of the sublattice symmetry can then only be investigated, when several F atoms per unit cell are considered and  $CF_x^{AB}$  is used for a system with both A and B carbon atoms chemically bonded with the F atom. The stability of unilaterally fluorinated graphene as a function of the concentration of fluorine and its position relative to the graphene lattice has been studied in detail in [10]. The most stable structure with one-sided adsorption is observed at  $x = 0.25$ , i.e. for the structure  $CH_{0.25}$  [11, 12]. The fluorine functionalization of graphene deforms the planar structure and modifies hybridization of the C–C bonds. The hybridization can be investigated by structural parameters such as a F–C distance and C–C bond angles (for C involved in the C–F bonds). The optimized atomic structure of  $C_8F_2^{AA}$  is depicted in Fig. 1. The C1–C2 bond length is 1.411 Å, and the C1–F bond length is 1.463 Å. The F–C1–C2 angle is about  $119.9^\circ$ , the C1–C2–C1 angle is about  $121.3^\circ$ , and the C1–F–C2 angle is about  $115.3^\circ$ .



**FIGURE 1.** Optimized atomic structure of  $C_8F_2^{AA}$ , which is formed by two F atoms adsorbed on second nearest neighbor on single side graphene. C and F atoms are presented by black and light circles (balls).

We now turn to analysis of the band structures (BS) of the CF systems. The electronic behavior strongly depends on the arrangement of the F atoms in the unit cell. Figure 2 shows the band structures of various graphene structures, which adsorbed the F atoms: (a) is the band structure for the system with a single adatom F in the supercell of graphene  $3 \times 3 CF_{0.125}$ , (b) and (c) are the band structures for the systems with two F adatoms in the supercell of graphene  $3 \times 3 CF_{0.111}^{AA}$  and  $CF_{0.111}^{AB}$ , respectively; (d) and (e) are the band structures for the systems with three adatoms F in the supercell of graphene  $3 \times 3 CF_{0.167}^{AAA}$ ,  $CF_{0.167}^{AAB}$ , respectively; (f), (g) and (h) are the band structures for the systems with four adatoms F in the supercell of graphene  $3 \times 3 CF_{0.222}^{AAAA}$ ,  $CF_{0.222}^{AABB}$  and  $CF_{0.222}^{AABB}$ , respectively; (i) and (k) are the band structures for the systems with two adatoms F in the supercell of graphene  $2 \times 2 CF_{0.25}^{AA}$  and  $CF_{0.25}^{AB}$ , respectively. As can be seen from Fig. 2, the band structure depends not only on the adatom F concentration, but also on the



**FIGURE 2.** Band structures of (a)  $CF_{0.125}$ , (b)  $CF_{0.111}^{AA}$ , (c)  $CF_{0.111}^{AB}$ , (d)  $CF_{0.167}^{AAB}$ , (e)  $CF_{0.167}^{AAA}$ , (f)  $CF_{0.222}^{AAAA}$ , (g)  $CF_{0.222}^{AABB}$ , (h)  $CF_{0.222}^{AABB}$ , (i)  $CF_{0.25}^{AA}$ , (k)  $CF_{0.25}^{AB}$ .

sublattice, to which the adatom is attached. For example,  $CF_{0.125}$ ,  $CF_{0.111}^{AA}$ ,  $CF_{0.111}^{AB}$ ,  $CF_{0.167}^{AAA}$ ,  $CF_{0.167}^{AAB}$ ,  $CF_{0.167}^{AAB}$  and  $CF_{0.25}^{AA}$  have almost flat bands crossing the Fermi level. These systems are metallic.  $CF_{0.222}^{AAAA}$ ,  $CF_{0.222}^{AABB}$  and  $CF_{0.25}^{AB}$  are semiconducting, with gaps of 0.06 eV, 0.11 eV and 2.7 eV, respectively.

## SUMMARY

We have employed the first-principles method within the density functional theory to study the structural and electronic properties of the fluorinated graphenes with different coverage of fluorine. It is revealed that the electronic properties of graphene can be modified by the absorption of different amounts of fluorine adatoms. Graphene is a nonmagnetic semimetal, which can be transformed into either a semiconductor or a metal, depending on the concentration of the adsorbed fluorine adatoms. The present study suggests that the adsorption of fluorine on the surfaces of graphene is a promising approach to modify the properties of graphene.

## REFERENCES

- [1] A. Geim and K. Novoselov, *Nat. Mater.* **6**, 183–191 (2007).
- [2] J. Pendry, *Science* **315**, 1227–1227 (2007).
- [3] M. Popinciuc, C. Jozsa, P. Zomer, N. Tombros, A. Veligura, and H. Jonkman, *Phys. Rev. B* **80**, 214427–214440 (2009).
- [4] J. Seol, I. Jo, A. Moore, L. Lindsay, Z. Aitken, M. Pettes, X. Li, Z. Yao, R. Huang, D. Broido, N. Mingo, R. Ruoff, and L. Shi, *Science* **328**, 213–216 (2010).
- [5] J. C. Charlier, X. Gonze, and J. Michenaud, *Phys. Rev. B* **47**, 16162–16168 (1993).
- [6] M. Klintenberg, S. Lebegue, M. Katsnelson, and O. Eriksson, *Phys. Rev. B* **81**, 085433–085438 (2010).
- [7] O. Leenaerts, H. Peelaers, A. Hernandez-Nieves, B. Partoens, and F. Peeters, *Phys. Rev. B* **82**, 195436–195442 (2010).
- [8] A. Markevich, R. Jones, and P. Briddon, *Phys. Rev. B* **84**, 125439–115445 (2011).
- [9] S. Cheng, K. Zou, F. Okino, H. R. Gutierrez, A. Gupta, N. Shen, P. C. Eklund, J. O. Sofo, and J. Zhu, *Phys. Rev. B* **81**, 205435–205440 (2010).
- [10] W. Lee, J. Suk, H. Chou, J. Lee, Y. Hao, Y. Wu, R. Piner, D. Akinwande, K. Kim, and R. Ruoff, *Nano Letters* **12**, 2374–2378 (2012).
- [11] F. Withers, T. Bointon, M. Dubois, S. Russo, and M. Craciun, *Nano Letters* **11**, 3912–3916 (2011).
- [12] H. Santos and L. Henrard, *J. Phys. Chem. C* **118**, 27074–27080 (2014).
- [13] Z. Wang, S. Qin, C. Wang, and Q. Hui, *Comput. Mater. Sci.* **97**, 14–19 (2015).
- [14] H. Liu, Z. Hou, C. Hu, Y. Yang, and Z. Zhu, *J. Phys. Chem. C* **116**, 18193–18201 (2012).
- [15] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, C. C. Roberto Car, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. F. G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter* **21**, 1–19 (2009).
- [16] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188–5192 (1976).