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# First-principles investigation of bilayer fluorographene

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*Ab initio* calculations within the density-functional theory formalism were performed to investigate the stability and electronic properties of fluorinated bilayer graphene (bilayer fluorographene). A comparison is made to previously investigated graphane, bilayer graphane and fluorographene. As expected, bilayer fluorographene is found to be a much more stable and robust material than bilayer graphane. Its electronic properties are similar to monolayer fluorographene but its electronic band gap is significantly larger (about 1 eV). We also calculate the effective masses around the  $\Gamma$ -point for fluorographene and bilayer fluorographene.

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## I. INTRODUCTION

Since the first reports on the successful isolation of stable two-dimensional crystals up to the thickness of only one atom by Novoselov *et al.* in 2004,<sup>1,2</sup> researchers have been looking for ways to employ these new materials in real-world applications. Special interest goes towards graphene, a single layer from the three-dimensional counterpart, graphite, which has high crystal quality and very promising electronic properties.<sup>3</sup>

Despite its unique characteristics which might be exploited in future applications,<sup>4–6</sup> there exists a serious obstacle to use graphene in electronics as we know it today. Graphene is a zero-gap semiconductor and this absence of a band gap is protected by inversion and time-reversal symmetry.<sup>7</sup> Several approaches to open and control a band gap in graphene and graphene derivatives can be distinguished: i) mechanical modification such as cutting the graphene sample into nanoribbons,<sup>8,9</sup> ii) application of a potential difference over a bilayer of graphene<sup>10,11</sup> and, finally, iii) chemical modification which confines the  $p_z$  electrons into covalent bonds.<sup>12–15</sup> The last approach includes the adsorption of radicals such as oxygen, hydrogen and fluorine atoms on the surface of graphene which form chemical bonds with the carbon atoms and change their hybridization from  $sp^2$  to  $sp^3$ .<sup>16</sup> The chemical derivatives of graphene preserve the two-dimensional character of graphene but they have vastly different electronic properties. This makes them possibly more interesting materials for the usual applications in electronics than intrinsic graphene.

Among the possible derivatives of graphene there are two that attract special attention, namely graphane and fluorographene (graphene fluoride), which result from the hydrogenation and fluorination of graphene, respectively. They are theoretically predicted<sup>16–20</sup> and experimentally observed<sup>12–14,21,22</sup> to form crystalline materials in contrast to e.g. graphene oxide.<sup>23,24</sup>

These new two-dimensional crystals are currently the subject of a considerable amount of experimental and theoretical work. But the process of chemical modification is not restricted to monolayer graphene. It has

been proposed that this process can be expanded to bilayer graphene as well.<sup>25</sup> *Ab initio* calculations show that in that case the weak van der Waals forces between the graphene layers are replaced by much stronger covalent bonds that stabilize the structure and that, at full coverage, a bilayer analogue of graphane is formed. The electronic structure of intrinsic monolayer and bilayer graphene are very similar,<sup>25</sup> but their mechanical/elastic properties are expected to be substantially different.

This last observation can be an important issue because it was recently demonstrated<sup>26</sup> that the roughness of monolayer graphene surfaces is considerably larger than that of graphene. This increase of the size of the ripple formation can be explained by the lower stiffness of graphane<sup>16</sup> and its different vibrational properties as compared to graphene.<sup>27</sup> One way to reduce the increased roughness is to consider bilayers instead of single layers. As is well known from experiment the ripple formation in bilayer graphene is almost completely removed by the interlayer interaction. A similar effect can be expected for bilayer graphane where the interlayer interaction is even more important.

In this paper we will investigate whether it is also possible to fluorinate bilayer graphene. We perform *ab initio* calculations to determine the stability and structural properties of a fluorinated bilayer of graphene, hereafter called bilayer fluorographene (for a better notion of the chemical composition and the structure see Fig. 2). We find that bilayer fluorographene is a much more stable compound than bilayer graphane, although more fluorination is needed to induce interlayer C-C bonds. The structural properties of bilayer fluorographene are in between those of monolayer fluorographene and diamond, other characteristics are closer to initial fluorographene.

This paper is organized as follows: first we describe the computational details of our *ab initio* calculations, followed by an investigation of the stability and the formation conditions of interlayer C-C bonds. Next, the overall stability and the geometrical properties of fully fluorinated bilayer graphene (i.e. bilayer fluorographene) are examined. These properties are subsequently compared with those of diamond and fluorographene. To conclude, we investigate the electronic band structure

and band gaps of single layer and bilayer fluorographene, together with the effective masses of the various possible charge carriers.

## II. COMPUTATIONAL DETAILS

All our calculations were done within the density functional theory (DFT) formalism as implemented in the VASP package with usage of the local-density approximation (LDA) for the exchange-correlation functional and the generalized gradient approximation (GGA) of the type Perdew, Burke and Ernzerhof<sup>28</sup> (PBE). We made use of the projector augmented wave method<sup>29</sup> and a plane-wave basis set with an energy cutoff of 500 eV. The relaxation of atomic positions was performed with forces less than  $0.01 \text{ eV } \text{\AA}^{-1}$ .

Two types of supercells were used in our calculations: i) a  $3 \times 3$  supercell to study the adsorption properties of fluorine on a graphene bilayer for different concentrations of fluorine, and ii) a  $1 \times 1$  unit cell for the calculation of the properties and electronic band structure of fully fluorinated graphene and bilayer graphene.

The sampling of the Brillouin zone was done for the different supercells with the equivalent of a  $24 \times 24 \times 1$  Monkhorst-Pack<sup>30</sup>  $k$ -point grid for the monolayer or bilayer graphene unit cell (containing 2 carbon atoms in each layer). Spin polarization was not included in the calculations because fluorination is not expected to induce magnetism in graphene.<sup>31</sup> Since periodic boundary conditions were applied in all three dimensions the height of the supercell was set to 20 Å to include enough vacuum to minimize the interaction between adjacent layers.

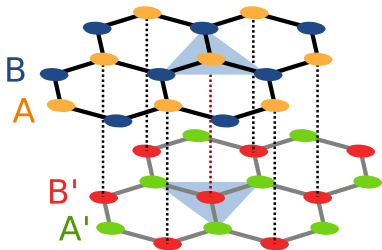


FIG. 1: (Color online) Bilayer of AB stacked graphene with the 4 different sublattices indicated by different shades (colors). The A and B' sublattice are situated on top of each other as illustrated by the dotted lines. The carbon atoms at the corners of the light triangles indicate the 6 neighbors to be fluorinated.

## III. FLUORINATION OF BILAYER GRAPHENE

The main objective of this paper is to investigate chemisorption of fluorine atoms on both sides of bilayer graphene. As has been found in earlier first-

principles calculations, hydrogenation and fluorination of the carbon atoms of graphene changes their hybridization from  $sp^2$  to  $sp^3$ .<sup>25</sup> In the case of hydrogenation of bilayer graphene, it was demonstrated that this induces stable interlayer C-C bonds at high concentrations of adsorbates.<sup>25</sup> In this section, we perform a similar study for the case of fluorination and highlight the similarities and differences as compared to hydrogenated bilayer graphene. We make use of the local density approximation here, because this approximation gives a better description of the interlayer interaction in bilayer graphene.<sup>25</sup>

We only consider chemisorption on bilayer graphene with AB-stacking because this is the most energetically favorable way of stacking graphene layers. As indicated in Fig. 1, this gives rise to four sublattices (2 in each layer) of which two, namely the A and B' sublattice, are exactly aligned on top of each other while the other two, i.e. B and A', are not. Since the adsorbates under investigation always chemisorb on top of a single C atom, there are two (inequivalent) adsorption sites, namely on the A (or B') sublattice and on the B (or A') sublattice. It was found in an earlier study of hydrogen adsorption on bilayer graphene that there is a difference in adsorption energy of approximately 0.03 eV in favor of the B sublattice.<sup>25</sup> The H atoms are therefore likely to attach to those carbon atoms which have no direct neighbors in the other layer. For F atoms, we find the same preference for adsorption on the B sublattice. However, the difference in adsorption energy for the two sublattices is only 0.3 meV, which is about 100 times smaller than in the case of hydrogen. This is probably caused by the partly different nature of C-F bonds as compared to C-H bonds: C-H bonds are purely covalent, but C-F bonds have a partially ionic character because of the large difference in electronegativity between C and F.

The formation of a chemical bond between an adsorbate and a C atom of the bilayer of graphene induces a change in the hybridization of this C atom from  $sp^2$  to  $sp^3$ . If the concentration of attached adsorbates on the preferred sublattice increases, the carbon atoms of the other sublattice also change their hybridization to  $sp^3$ . This allows for the formation of covalent bonds between the two graphene layers.<sup>25</sup> These interlayer bonds are formed between carbon atoms of the A and B' sublattices that are pushed to one another because of the changed hybridization of their neighbors.

For one interlayer C-C bond there are six neighbors - three atoms in the B and three in the A' sublattice (Fig. 1). However, it is not necessary for all these neighbors to change their hybridization in order for the interlayer bond to be formed: E.g. in the case of hydrogen chemisorption on bilayer graphene, only four of the neighboring carbon atoms need to be hydrogenated to induce a covalent interlayer bond.<sup>25</sup>

In order to study the formation of interlayer bonds upon fluorination in more detail, we gradually increase the number of attached fluorine atoms on neighboring

carbon atoms from 1 to 6. We completely relax the resulting systems and calculate the average and minimum distance between the C atoms of the two layers. The results of these computations are summarized in Table I. From this table, a gradual decrease of the interlayer distance can be seen upon increasing the concentration of F atoms. At higher concentrations, however, a substantial jump in the minimum distance,  $d_{min}$ , occurs when going from 4 to 5 fluorinated neighbors. This jump is about 1 Å in size and clearly indicates the formation of an interlayer bond. It is thus necessary to fluorinate 5 of the 6 neighbors to induce an interlayer bond, in contrast to hydrogenation where 4 hydrogenated neighbors suffice.

TABLE I: Interlayer chemical bond formation in a  $3 \times 3$  supercell. The binding energy per F atom ( $E_b$ ), the formation energy per F atom ( $E_f$ ) and the average ( $d_{avg}$ ) and minimum distance ( $d_{min}$ ) between the C atoms of the two layers are shown for different number of adsorbed fluorine atoms and different configurations. Presence of interlayer bond is marked as chemical bond. Energies are given in eV and distances in Å.

# F atoms	configuration	$E_b$	$E_f$	$d_{avg}$	$d_{min}$	chem. bond
1	<i>B</i>	-2.525	-0.819	3.326	3.256	no
2	<i>BB</i>	-2.405	-0.700	3.326	3.190	no
2	<i>BA'</i>	-2.555	-0.850	3.213	3.085	no
3	<i>BBB</i>	-2.290	-0.585	3.332	3.126	no
3	<i>BBA'</i>	-2.487	-0.782	3.176	2.979	no
4	<i>BBBA'</i>	-2.384	-0.679	3.150	2.903	no
4	<i>BBA'A'</i>	-2.479	-0.773	3.061	2.821	no
5	<i>BBBA'A'</i>	-2.450	-0.745	2.678	1.757	yes
6	<i>BBBA'A'A'</i>	-2.560	-0.854	2.598	1.737	yes

Additional information about the stability of the interlayer bond can be obtained by examining the formation and binding energy of the system at different concentrations of adsorbed F atoms. We define the formation energy ( $E_f$ ) as the energy per attached fluorine atom with respect to intrinsic bilayer graphene and the diatomic molecule  $F_2$ . The binding energy ( $E_b$ ), on the other hand, is defined as the energy per fluorine atom (or CF pair) with respect to intrinsic bilayer graphene and atomic fluorine. Both energies are given in Table I.

The formation energy,  $E_f$ , is negative in all cases which means that all the configurations are stable against molecular desorption from the graphene surface. This should be contrasted to the same concentrations of hydrogen atoms on the surface of bilayer graphene, where the energy becomes negative only in the case of almost fully hydrogenated bilayer graphene.<sup>25</sup> The value of the formation energies in the case of fluorination is significantly lower (almost 1 eV) than in the case of hydrogen chemisorption. This can be attributed to the higher binding energy of  $F_2$  as compared to  $H_2$  molecules and is similar to what has been observed previously for the case of monolayer graphene and fluorographene.<sup>16,20</sup> The

calculated binding energies also show that it is energetically favorable for the fluorine atoms to attach themselves on both sides of the bilayer: for the same number of chemisorbed F atoms, the configuration in which these atoms are distributed as equally as possible between the two layers is lower in energy and thus more stable. The fact that adsorbed fluorine atoms on one side of the bilayer make it favorable for other F atoms to adsorb on the other side, increases the chance of interlayer bond formation. Because these bonds are stable, we can imagine this process of fluorination and interlayer bond formation to continue until a fully covered bilayer of graphene fluoride is formed.

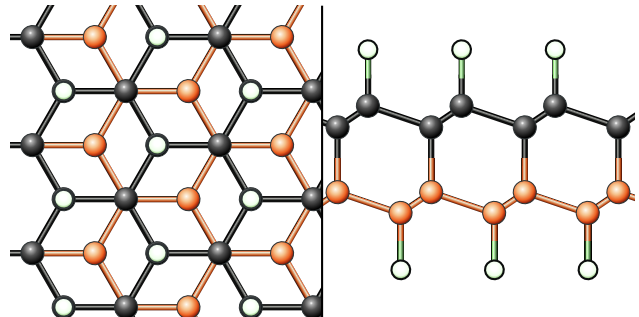


FIG. 2: (Color online) Top (left) and side (right) view of bilayer fluorographene. The carbon atoms of the two layers are given different colors (shades) for clarity and the fluorine atoms are in light green (open circles with the smallest diameter).

#### IV. PROPERTIES OF BILAYER FLUOROGRAPHENE

In this section we will examine the properties of bilayer fluorographene in more detail and compare them with those of monolayer fluorographene and diamond. For the study of the geometrical properties we include also GGA calculations because they give more accurate bond lengths and angles. A summary of the geometrical and electronic properties is given in Table II and III. The results for monolayer fluorographene compare well with previous calculations on this system.<sup>16,19</sup> As can be expected, the cell size, bond lengths and angles of bilayer fluorographene have values between those of monolayer fluorographene and diamond. Due to the ionic character of the C-F bond the neighboring C-C bonds are longer than the ones in diamond as was observed previously.<sup>16</sup> Another consequence of this ionic bond character is the shortening of the C-F bond with increasing amount of fluorination on both sides of bilayer fluorographene: in a  $3 \times 3$  supercell, we were able to observe a variation of the C-F bond length from 1.50 Å for configuration *B* to 1.43 Å for configuration *BBBA'A'A'*. As can be seen from Table II, the C-F bond length decreases even more to 1.38 Å for fully fluorinated bilayer graphene.

TABLE II: Properties of single layer and bilayer fluorographene: the unit cell length ( $a$ ), the distances ( $d$ ) and angles ( $\theta$ ) between neighboring atoms. Distances are given in Å and angles in deg.

	fluorographene		bilayer fluorographene		diamond	
	LDA	GGA	LDA	GGA	LDA	GGA
$a$	2.555	2.596	2.525	2.563	2.499	2.527
$d_{C-C}$	1.553	1.576	1.541	1.563	1.531	1.547
$d_{C-C'}$	n/a	n/a	1.537	1.554	1.531	1.547
$d_{C-F}$	1.365	1.382	1.361	1.377	n/a	n/a
$\theta_{CCC}$	110.7	110.9	110.0	110.2	109.5	109.5
$\theta_{CCC'}$	n/a	n/a	108.9	108.7	109.5	109.5
$\theta_{CCF}$	108.2	108.0	108.9	108.7	n/a	n/a

The electronic properties of monolayer and bilayer fluorographene are given in Table III: we calculated the band gaps of these materials together with the formation energies per atom (in contrast to previously used formation energies per fluorine atom) For comparison, the values of these quantities are also given for diamond.

The calculated band gap for monolayer fluorographene is in good agreement with previously published results for GGA calculations.<sup>16,32</sup>

Although the computed band gap value for fluorographene is close to experimental measured values,<sup>12</sup> this should be seen as a coincidence. LDA and GGA calculations are known to largely underestimate the value of the band gap. The calculated band gaps are in fact two times lower than more accurate results of many-electron GW calculations.<sup>20</sup> This apparent discrepancy has been attributed to the presence of a considerable amount of defects in the experimental samples.<sup>16</sup>

The band gap of bilayer fluorographene is found to be larger than the one of monolayer fluorographene by approximately 1 eV. This is different from the case of hydrogenated graphene where monolayer graphane is found to have a slightly larger band gap than bilayer graphane.<sup>25</sup> Although our calculations are not accurate enough to provide the real band gap, it is probable that this difference in the size of the band gap between monolayer and bilayer fluorographene is qualitatively correct. This follows from the fact that LDA and GGA usually produce correct trends in the variation of the band gap among similar systems.

The formation energy of bilayer fluorographene is larger than the the one of the monolayer but still closer to it than to the value of diamond. The main reason for the observed weakening of the formation energy is the drop of the ratio of the amount of fluorine atoms per carbon atom in going from monolayer to bilayer fluorographene. Overall, the qualitative image of the stability of the fluorinated materials corresponds to that of graphane and bilayer graphane<sup>25</sup> but there is a large quantitative difference in that the fluorinated materials are much more

stable structures than the hydrogenated ones.

TABLE III: Electronic band gap  $E_{gap}$  and formation energy per atom ( $E_f/atom$ ) of monolayer and bilayer fluorographene and diamond for LDA and GGA calculations. All the energies are given in eV.

	fluorographene		bilayer fluorographene		diamond	
	LDA	GGA	LDA	GGA	LDA	GGA
$E_{gap}$	2.960	3.089	3.951	4.040	5.618	5.572
$E_f/atom$	-1.057	-0.944	-0.722	-0.593	-0.011	0.132

The band structure of monolayer and bilayer fluorographene is displayed in Fig. 3 followed by a diagram of the density of states in Fig. 4 The depicted band structures are seen to be qualitatively similar with the size of the band gap as the only obvious difference. We also calculated the effective masses of the possible charge carriers around the  $\Gamma$ -point in order to find other differences or similarities between the two materials.

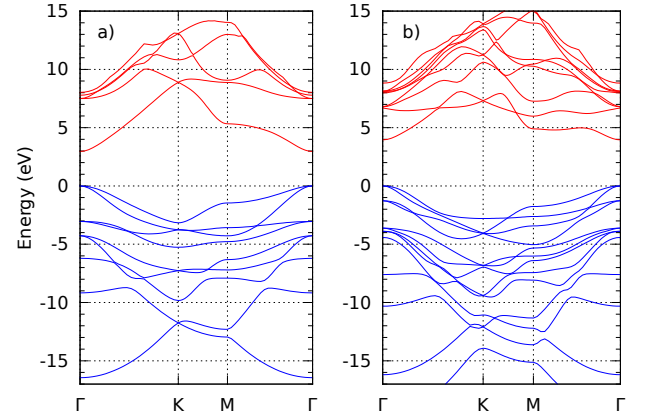


FIG. 3: (Color online) The electronic band structure of monolayer (a) and bilayer (b) fluorographene. The energies are relative to the Fermi level ( $E_F=0$ ).

The obtained effective masses of electrons, and heavy and light holes for both studied materials, can be found in Table IV. The effective mass of charge carriers in crystalline materials usually depends on the direction in reciprocal space. Therefore we have chosen two common directions for hexagonal lattice at the  $\Gamma$ -point, namely:  $\Gamma \rightarrow K$  and  $\Gamma \rightarrow M$ . The results for these two directions were found to be indistinguishable and so we can conclude that the effective masses at the  $\Gamma$ -point are isotropic. It should be noted that the direction independence for the effective masses that we observe contradicts previous results in which the effective masses of monolayer fluorographene were found to be highly anisotropic.<sup>33</sup>

Our statement about the isotropic character of the effective masses is supported by a direct plot of the energy value map around the  $\Gamma$ -point. In Fig. 5 we show

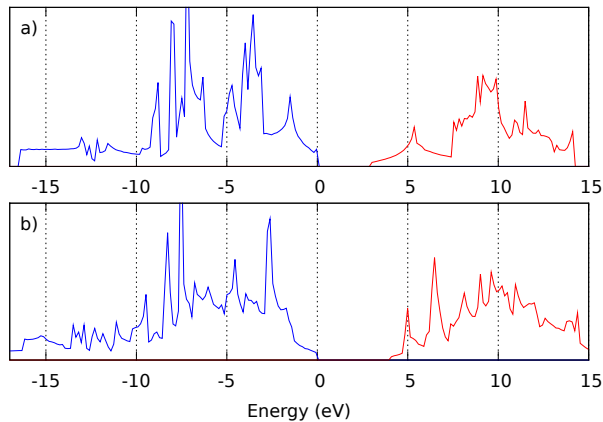


FIG. 4: (Color online) The density of states of monolayer (a) and bilayer (b) fluorographene. The energies are relative to the Fermi level ( $E_F=0$ ).

a picture of the highest valence band of monolayer fluorographene. The isotropic character of this band is clearly visible close to the  $\Gamma$ -point. Farther away from the  $\Gamma$ -point an anisotropy of the surface map is visible which can be attributed to fourth and higher order effects. However, these higher order effects do not induce anisotropy in the effective mass which is a second order effect. Similar results are found for the light hole and the electrons.

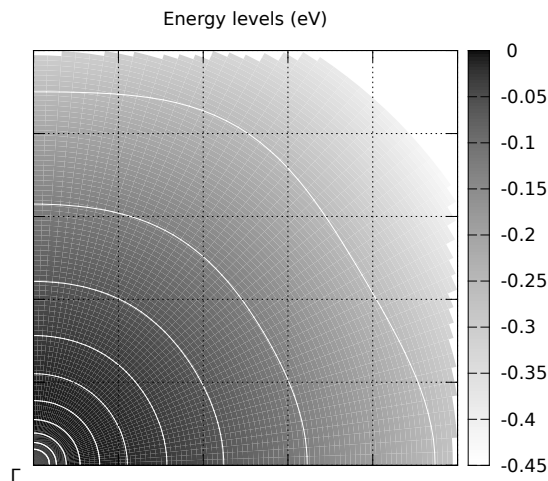


FIG. 5: Energy levels of the highest valence band of monolayer fluorographene in reciprocal space. The displayed region is a squared portion of the Brillouin zone with a side length 0.22 of the  $\Gamma$ -M distance. The  $\Gamma$ -point is taken as the origin and the x-axis directed towards the M-point. Contour lines are displayed for a better notion of the symmetry.

When we compare the effective masses of monolayer and bilayer fluorographene, we observe only a small difference in the values. We therefore conclude that both materials have similar electronic properties apart from a difference in the band gap of about 1 eV.

TABLE IV: Effective masses of holes and electrons (in units of the electron mass).

	fluorographene	bilayer fluorographene
$m$	0.48	0.50
$m_{hh}$	1.13	1.10
$m_{lh}$	0.41	0.37

## V. SUMMARY AND CONCLUSIONS

As an extension of previous work<sup>16,25</sup> we studied the potentially interesting case of bilayer fluorographene. We demonstrated that fluorination of bilayer graphene results in more stable structures than hydrogenation. The creation of interlayer chemical bonds occurs at higher amounts of fluorination as compared to hydrogenation.

The calculated band gap of bilayer fluorographene shows a 30% increase over the one of bilayer graphene, and we also observed quantitatively significant differences between monolayer and bilayer fluorographene. The observed trend is likely to prevail even for the real values or more accurate GW calculations.

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