Electronic Structures, Bonding Configurations, and Band-Gap-Opening Properties of Graphene Binding with Low-Concentration Fluorine

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To better understand the effects of low-level fluorine in graphene-based sensors, first-principles density functional theory (DFT) with van der Waals dispersion interactions has been employed to investigate the structure and impact of fluorine defects on the electrical properties of single-layer graphene films. The results show that both graphite-2H and graphene have zero band gaps. When fluorine bonds to a carbon atom, the carbon atom is pulled slightly above the graphene plane, creating what is referred to as a C_f defect. The lowest-binding energy state is found to correspond to two C_f defects on nearest neighbor sites, with one fluorine above the carbon plane and the other below the plane. Overall this has the effect of buckling the graphene. The results further show that the addition of fluorine to graphene leads to the formation of an energy band (B_f) near the Fermi level, contributed mainly from the 2p orbitals of fluorine with a small contribution from the p orbitals of the carbon. Among the 11 binding configurations studied, our results show that only in two cases does the B_f serve as a conduction band and open a band gap of 0.37 eV and 0.24 eV respectively. The binding energy decreases with decreasing fluorine concentration due to the interaction between neighboring fluorine atoms. The obtained results are useful for sensor development and nanoelectronics.

Introduction

In the area of energy applications, graphene and graphene-based nanomaterials have many promising applications.[1] These include sensors,[2] solar cells,[3] supercapacitors,[4] batteries,[5] and catalysis.[6] Applications in micro- and nanoelectronics[7] are also of great interest. As an underpinning for the development and use of graphene in these areas, a detailed theoretical understanding of the electronic structure of graphene is required. To this end, a considerable level of effort has been expended over the last few years.[8] As a result, there is a reasonably solid understanding of the electronic structure and electrical properties of "ideal" or pure graphene sheets.

Although pure graphene sheets serve as a conceptual starting point, defects, native and intentional, may play a critical role in modifying and possibly optimizing graphene properties in a given application. Chemisorbed adatoms are perhaps the most common and facile means of introducing defects to the graphene structure. Examples of naturally occurring defects of this type include the hydroxide and epoxide groups found on graphene oxide and reduced graphene oxide.[9] Examples of intentional defects include metal,[10] hydrogen,[11] and halogen adatoms.[12] The experimental efforts to characterize these defects have been accompanied by even more robust theoretical efforts to understand their impact on the electrical properties of graphene.[13]

Members of our research team have recently reported a novel method for synthesis of epitaxial graphene films that involves halogen-based plasma etching of SiC followed by ultrahigh vacuum annealing.[14] This produces single and multilayer graphene films with a halogenated defect whose concentration can be controlled by the annealing temperature. Using nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS), Ito and co-workers[15] have identified a similar defect in fluorine-graphite intercalation compounds (F-GICs). More recently, Meyer–Plath and co-workers[12a] have identified an analogous defect in brominated graphitic materials, including graphene. Molecular level modeling results were used by Friedrich et al. to show that these defects buckle the graphene surface.[16]

As a special semiconductor, graphene is a single-layer graphite sheet. Similar to graphite, due to its orthogonal $\pi$ and $\pi^*$ orbitals which do not overlap each other and only touch at six points (Dirac Points), the graphene acts as a zero-band-gap semimetal. Such Dirac-cone band structure possesses linear energy-momentum dispersion near Fermi level ($E_F$) to exhibit

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/open.201500074. The total density of states (TDOS) and partial density of states (PDOS) of 2F-adsorbed graphene for cases A, B, D, and E with eight configurations are given.

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zero rest mass with Hall Effect. Therefore, the massless electrons in graphene with a Fermi velocity (∼10^6 m s^-1) are very useful in electronic applications, such as high-frequency transistors and ultrafast photodetectors. However, such zero-band-gap nature results in high leakage currents and power dissipation, limiting its applications. Hence, introducing a band gap in graphene through band-structure engineering is highly useful for many applications. Creating defects and covalent binding with other atoms or molecules are effective ways to open the band gap on the zero-gap of pristine graphene. In the literature, many theoretical studies were focused on fully or partially halogenated/hydrogenated graphene, such as C_xF_y, C_xCl_y, C_xBr_y, and C_xI_y, (Y = Cl, Br, I) [18a, 23]. These systems, where the carbons of graphene are sp^2 hybridized and more than 25% of them were saturated by halogen or hydrogen atoms, were quite different from the planar 2D graphene with sp^2 hybrid orbitals to bond with neighboring carbon, and, as a result possess large band gaps (∼8 eV). In contrast, little investigation has been performed on graphene bonding with a low concentration of adatoms (<5%) to understand the bonding configuration and conditions for band-gap opening.

The research described in this paper is aimed at a more complete understanding of the structure of low-concentration halogenated defects in single layer graphene films and the impact of these defects on the electronic properties. The approach taken here used first-principles density functional theory (DFT) to first investigate the binding sites of fluorine on graphene and then explore the effects of fluorine concentration. The next section of the paper briefly describes the theoretical methods, while the following section presents the pure and fluorine-adsorbed graphene are presented. The last section summarizes the major results and conclusions.

## Results and Discussion

### Bonding configurations

As shown in Figure 1, the graphene structure can be created by cleaving parallel to the (001) surface of graphite-2 H. Figure 2 shows the relationship of the graphene crystal lattice constant (a = b) and the corresponding lattice total energy. For comparison, the data with and without van der Waals (VDW) dispersion interactions are plotted in the figure. As can be seen, these relationships fit well with the polynomial $E(a) = B_0 + B_1a + B_2a^2$, where the coefficients $B_0$, $B_1$, and $B_2$ are shown in Figure 2. Although the VDW interaction lowers the total energy by about 0.1 eV, the predicted equilibrium crystal constants from both methods are very close to each other with values of 2.4684 Å (without VDW) and 2.4683 Å (with VDW). These results indicate that the VDW interaction could affect the total energy, but does not change the structure of graphene.

Table 1 summarizes the optimized crystal constants and total electronic energies ($E_a$) of graphene and graphite-2H. Compared to graphene which has no interlayer interaction because of its larger interlayer distance ( computationally fixed at 30 Å), graphite has a stronger interlayer interaction due to a shorter layer distance of 3.722 Å. Obviously, it can also be seen from Table 1 that the graphite-2H has a larger VDW contribution (−0.46 eV) to its $E_a$ than graphene (−0.13 eV).

In order to reach the experimentally observed F-adsorption level of 2%, a 7×7×1 surface was generated from graphite-2H crystal to represent graphene in our following calculations.

![Figure 1. The graphene structure created by cleaving graphite-2H (space group P63/mmc (#194) parallel to the (0001) surface and adjusting to the calculated equilibrium crystal constant.](Image)

![Figure 2. The calculated total energy versus the crystal constant in graphene and without van der Waals interactions. The data were fitted into the polynomial $E(a) = B_0 + B_1a + B_2a^2$.](Image)
as shown in Figure 1. Figure 3 shows the 1F- and 2F-adsorbed graphene configurations which are used in this study. For two fluorine atoms binding on carbon of graphene (with the F-bonded carbon designated as Cb), there are many possible binding sites. Binding the first fluorine directly over a carbon atom (Fi site in Figure 3) produces what is referred to as a Cb defect. For the second F-binding site (Cb defect), one of five different cases (A, B, C, D, and E), as shown in Figure 3, was chosen. For each case, the two fluorine atoms can be on the same or opposite side of the graphene plane. This leads to two different configurations for each of the five cases.

Figure 4 shows the initial and optimized configuration for 1F-adsorbed graphene. As seen here, after binding with fluorine to form the Cb defect, the carbon atom was pulled about 0.5 Å above the graphene plane (see the Zb value in Table 2). As a result the F–Cb–C bond angle becomes 102.4°. This represents a 12.4° deviation from the initial bond angle of 90°, and is approaching the 109.5° bond angle associated with sp² hybridization. In addition, the optimized F–Cb bond length (rb) is 1.575 Å. The binding energy (Eb) of fluorine on graphene, which is calculated as the energy difference between the optimized F-bonded configuration and the individual pure graphene and a single fluorine atom in a 20x20x20 box, is −2.07 eV. This indicates the chemical bonding of F–Cb is very strong, as expected.

The optimized structures for 2F-adsorbed graphene are shown in Figure 5 and summarized in Table 2. Obviously, in all five cases, when the second fluorine is on the same side of the graphene plane, the Cb is significantly pulled out of the plane. Such phenomena have also been observed by other researchers. One overall effect of these Cb defects is to buckle the otherwise flat graphene layer. However, when the second fluorine binds on the opposite side of the graphene plane, the Cb are less significantly pulled out of graphene plane. As one can see that the amount of Cb buckling (Zb) from graphene plane highly depends on the two F-binding configurations. When the separation of 2F is far enough (cases D and E), the Zb value does not change too much for both configurations. As seen from Table 2 and Figure 5, except for case C, the binding energy of 2F-adsorbed graphene is larger when the fluorine atoms are bonded on the opposite sides of the graphene plane. This is due to the effects of F-F repulsion. Obviously, the total binding energy (Eb) of 2F-adsorbed graphene depends

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Table 2. Binding energy (Eb), Cb buckling off the graphene plane (Zb), Cb–F bond length (rb), and F–Cb–C angles in 1F- and 2F-adsorbed graphene (G).

| F on same side of G | G-1F (case A) | G-2F (case B) | G-2F (case C) | G-2F (case D) | G-2F (case E) |
|---------------------|---------------|---------------|---------------|---------------|---------------|
| Eb [eV/1F]          | −2.071        | −2.225        | −1.913        | −2.301        | −1.976        | −2.158        |
| Zb [Å]              | 0.503         | 0.845         | 0.637         | 0.623         | 0.505         | 0.525         |
| rb [Å]              | 1.575         | 1.462         | 1.553         | 1.495         | 1.589         | 1.528         |
| F–Cb–C [°]          | 102.40        | 102.04        | 106.25        | 104.06        | 102.66        | 103.44        |

| F on opposite sides of G | G-2F (case A) | G-2F (case B) | G-2F (case C) | G-2F (case D) |
|--------------------------|---------------|---------------|---------------|---------------|
| Eb [eV/1F]               | −2.531        | −1.960        | −2.275        | −2.001        | −2.165        |
| Zb [Å]                   | 0.344         | 0.394         | 0.433         | 0.507         | 0.512         |
| rb [Å]                   | 1.474         | 1.592         | 1.517         | 1.599         | 1.534         |
| F–Cb–C [°]               | 104.16        | 104.66        | 102.22        | 102.77        | 103.21        |

[a] From Ref. [19].

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Electronic structural properties of graphene

Figure 6a gives the band structure of graphite-2H (space group P63/mmc (#196)). The total density of states (TDOS) and projected atomic partial density of states (PDOS) of graphite-2H are shown in Figure 7a. Since the graphite unit cell contains four carbon atoms, there are eight occupied bands in its valence band (VB). It can be clearly seen that the graphite-2H has zero band gap along the highly symmetrical H–K points, and its DOS is characterized by a very low value at the Fermi level $E_f$ which is in good agreement with other reported results.[26] From the PDOS shown in Figure 7a, it may be seen that the VB is composed of carbon s and p orbitals, with the s orbital dominating at lower energies, and the p orbitals being more pronounced at higher energies just below the Fermi-level $E_f$. The reason is that the s orbital of carbon participates in building up the $sp^2$ hybrids to form low-lying $\sigma$ bands as shown in Figure 6a, while the higher-lying $\pi$ bands have $p_z$ character only. The low value of the DOS at $E_f$ is also well documented from XPS measurements[27] and in other theoretical reports.[26a,28]

As a special semiconductor with zero band gap, graphene is a single-layer graphite sheet. Since the graphene unit cell contains two carbons, there are four bands in its valence band. Similar to graphite, the graphene also has a zero band gap as shown in Figure 6b.[8c,29] At the high-symmetry Γ point, there is a large gap of 6.3 eV; this is decreased to 4 eV at M point, and at K point the band gap is decreased to zero. These results are in good agreement with those predicted by tight-binding analysis.[26d] As shown in Figure 7b, the TDOS at Fermi level ($E_f$) also has a very low value of $3.5 \times 10^{-4}$ which confirms that its band gap is very close to zero. Similarly, the PDOS of graphene shows that the s orbital of carbon contributes to the lower energy states while its p orbitals contribute to the higher energy of the valence band which is active for fluorine binding.

Bonding properties of F-adsorbed graphene

Figure 8 shows the calculated TDOS and PDOS of 1F-adsorbed graphene. Compared to the pure graphene with zero band gap shown in Figure 7b, when fluorine binds with the carbon of graphene to form the C₁ defect, the electronic structure is changed. As shown in Figure 4, the optimized F–C₁ bond is not only on the F–C₁ (r_{CF}) bond length, but also on the buckling configuration of graphene. As one can see that among them, case A has shortest r_{CF} and largest $Z_{CS}$ hence possessing largest $E_b$.

Among all ten cases shown in Figure 5, case A has the largest binding energy. This corresponds to the situation where the Cₓ defects are on adjacent carbon atoms with one fluorine above the plane and the other below the plane. Of the configurations with both fluorine atoms located on the same side of the plane, case C₁ has the largest binding energy. Interestingly, the binding energy is larger when these two Cₓ defects have an odd number of C–C intervals between them (cases A, C, D) than those cases having even number of intervals (case B, E). The reason for this is that when the first Cₓ defect is formed, the charge distributions on the carbon atoms are no longer equal. When the second Cₓ defect is formed, the binding energy depends on the position of the Cₓ. In cases A, C, and D, there is a neighbor carbon to Cₓ which is almost directly aligned with the F–F repulsion, and which attracts the fluorine in the same direction as the repulsion. This is most apparent for configuration C₁. From Table 2, it can be seen that the binding configurations for 2F-adsorbed graphene with larger binding energies have shorter F–Cₓ bond lengths with stronger bonding. For cases A₁ and B₂, our calculated F–Cₓ bond lengths are slightly longer than the values reported by Bettinger et al.[19] due to different exchange-correlation functionals used in the calculations.

Figure 5. The optimized structures of 2F-adsorbed graphene with different binding configurations. The bond length and angles are also summarized in Table 2.
length is 1.575 Å, which indicates the bonding between fluorine and graphene is very strong, with a binding energy of 2.071 eV. Around the Fermi-level $E_F$, there is a new band which is mainly contributed by $p$ orbitals of fluorine atom. From the PDOS of carbon and fluorine shown in Figure 8, one can see that the contributions from the $p$ orbitals of carbon are located below the Fermi level, while a fluorine band ($B_F$), with a bandwidth of 0.36 eV, lies near the Fermi level and is partially occupied. Below the $B_F$ there is a small gap $E_{VBF}$ with a value of 0.12 eV, while above the $B_F$ there is a gap $E_g$ with a value of 0.378 eV between $B_F$ and the conduction band (CB).

The calculated energy gaps and band widths of $B_F$ for 2F-adsorbed graphene with the ten binding configurations are listed in Table 3. The calculated charges on fluorine and $C_F$ atoms are also listed in Table 3. Obviously, after bonding with $C_F$, fluorine obtains electrons from $C_F$ and its near neighbor carbon atoms. Since $C_F$ has $sp^3$ hybridization, and the nearest carbons possess $sp^2$–$sp^3$ crossover to fully $sp^2$-hybridized carbons, such structural change causes important distortion of the lattice (buckling the graphene).[13d] Both of these carbons donate electrons to fluorine atoms. Figure 9 shows the TDOS of all 2F-adsorbed graphene configurations around the $E_F$ region. The complete TDOS of these 2F-adsorbed graphene configurations are shown in Figure S1 in the Supporting Information. As an exam-
Table 3. Charges on fluorine and C$_2$, F-band ($B_1$) width, and gap between VB$_1$ and B$_1$ ($E_{	ext{VB}}$) of 1F- and 2F-adsorbed graphene (G).

| F on same side of G | G-1F | G-2F | G-2F | G-2F | G-2F | G-2F |
|---------------------|------|------|------|------|------|------|
|                     | (case A$_1$) | (case B$_1$) | (case C$_1$) | (case E$_1$) | (case D$_1$) |
| $E_{	ext{VB}}$ (eV) | 0.119 | 0.371 | 0.352 | 0.478 | 0.144 | 0.240 |
| $B_1$ width$^\text{[a]}$ | 0.359 | 0.124 | 0.587 | 0.120 | 0.471 | 0.359 |
| Charge on F         | -0.59 | -0.65 | -0.57 | -0.59 | -0.58 | -0.58 |
| Charge on C$_2$     | 0.33  | 0.55  | 0.39  | 0.51  | 0.49  | 0.48  |

| F on opposite sides of G | G-2F | G-2F | G-2F | G-2F |
|--------------------------|------|------|------|------|
|                         | (case A$_2$) | (case B$_2$) | (case C$_2$) | (case E$_2$) |
| $E_{	ext{VB}}$ (eV)     | 0.366 | 0.400 | 0.365 | 0.118 |
| $B_1$ width$^\text{[a]}$ | 0.122 | 0.582 | 0.121 | 0.353 |
| Charge on F              | -0.66 | -0.58 | -0.59 | -0.58 |
| Charge on C$_2$          | 0.56  | 0.32  | 0.43  | 0.44  |

$^\text{[a]}$ F-band width which is located between VB$_1$ and CB.

Table 3 shows the calculated electron densities of states (DOS) for 2F-adsorbed graphene. The gap between VB$_1$ and B$_1$ ($E_{	ext{VB}}$) is given for different configurations: A$_1$, A$_2$, B$_1$, B$_2$, C$_1$, C$_2$, E$_1$, and E$_2$. The $B_1$ width is also provided for each configuration. The calculated gaps are smaller than the measured values, which is due to the DFT approximations used. The authors conclude that the electronic structure of graphene in a manner that depends on the defect structures.

It should be pointed out that due to the DFT approximations, which underestimate the excited-state energies, the calculated band gaps are usually smaller than the experimentally measured values. Hence, our calculated band gaps may be smaller than the true values, but it does not affect the prediction of band-gap opening. It also needs to be pointed out that the electronic structure for pure graphene with the 7 x 7 x 1 supercell (Figures S1 and S2 in the Supporting Information) has some differences compared with the 1 x 1 x 1 unit cell (Figures 6b and 7b). This is particularly true with regard to their conduction bands (CBs). Although both of them have zero band gaps, in the supercell there is a clear peak (partially occupied) cross the Fermi level contributed mainly from p orbitals of the carbon atoms. Above this peak, there is a gap $E_g$ with a value of 0.5 eV. When electron-rich fluorine is adsorbed to graphene, most electrons of the fluorine atoms fill into this peak and separate it deeply from the nearest VB and CB depending on the specific adsorption site occupied.

From Figure 9 and Figure S1 in the Supporting Information, one can see that the electronic structures of 2F-adsorbed graphene are different for each of the ten configurations. For case A (Figure 3, 5, S3), where the $C_2$ defects are located on nearest neighbor sites, narrower $B_1$ widths and wider $E_{	ext{VB}}$ gaps were obtained as compared with case B where the $C_2$ defects are located on the next nearest neighbor sites (Figures 3, 5, and S4). Similar to pure and 1F-adsorbed graphene illustrated in Figures 7 and 8, the 2F-adsorbed configurations in case A (Figure 9 and S3) are also spin non-polarized, as their TDOS and PDOS for spin-up and spin-down are virtually the same. In case B (Figure S4a), however, where the two $C_2$ defects are located on second-nearest neighbors with the fluorine atoms on opposite sides of the graphene film, there are differences in the TDOS and PDOS for spin-up and spin-down which suggest that adsorption with fluorine could change the magnetic properties of graphene. In contrast, in the case of B$_{\text{I}}$ (Figure S4b), where the two fluorine atoms are on the same side of the graphene plane, there is very little difference in the spin-up and spin-down states. From Figure 9, it could be seen that in case B$_{\text{I}}$, band $B_{\text{I}}$ is partially occupied, while in case A$_{\text{I}}$, its $B_{\text{I}}$ is unoccupied and serves as a conduction band.

As discussed in previous sections and shown in Figure 5 and Table 2, the fluorine binding sites on graphene play an important role in the binding configurations and electronic properties. Such phenomena come from their different bonding environments and electronic structural properties. By comparing the TDOS of five binding sites (cases A-E) of 2F-adsorbed graphene as shown in Figure 9 and Figure S1 in the Supporting Information, it can be seen that there are significant differences between these configurations. In cases C and D (Figures 9, S1, 10, and S5), the gap $(E_{	ext{VB}})$ between VB$_1$ and B$_1$ is located...
around Fermi level $E_F$. This indicates that 2F-adsorption of graphene in configurations C and D could open a band gap (0.37 eV and 0.24 eV respectively). In case A, the TDOS around $E_F$ is very low (but not zero), and $B_F$ is fully unoccupied and serves as a CB. From Figures 9, S1, and S6, it can be seen that the two configurations for case E express opposite characteristics. When the fluorine atoms are bound on the same sides of the graphene plane (case $E_1$), $B_F$ is partially occupied. In contrast, when the fluorine atoms are bound on the opposite sides of the graphene plane (case $E_2$), $B_F$ is fully unoccupied.

As shown in Figure 6 and 7, in graphene, the $sp^2$ carbon atoms provide two orbitals ($\pi$ and $\pi^*$) to form VB and CB. Since these orthogonal $\pi$ and $\pi^*$ orbitals do not overlap with each other, the graphene has a zero band gap, which results in high leakage currents and power dissipation, and therefore limits its applications.\cite{17A} Hence band-structure engineering to open a band gap in graphene is expected to be very useful for many applications. Unlike fully or highly but partially fluorinated graphene, where the carbon is $sp^2$ hybridized, saturated by fluorine atoms, and possesses large band gaps (3–8 eV),\cite{18a–d,19–20} the computational results presented here show that low-percentage adsorption with fluorine also has the potential to open a band gap in graphene making possible an even wider range of applications. Our calculated results show that by adsorption with fluorine into graphene, the symmetry of the graphene unit cell is decreased. Therefore, the carbons can be distinguished in the unit cell, and more electrons from fluorine are introduced in the valence band. Such a chemical modification provides possible ways to open the band gap of graphene for wide applications.

As shown in Figures 9–10 and Figures S1–S6 in the Supporting Information, at low F-adsorption levels (~2%), only cases C and D have a band gap with values of 0.37 eV and 0.24 eV respectively. The other configurations still maintain zero band gap. Similarly, with local density approximation (LDA) and GW$_0$ approaches, Sahin et al.\cite{18b} calculated the electronic structures of fluorinated graphene (CF, C$_F$, C$_2$F) and their signatures. Their results showed that boat configuration of C$_2$F possesses a band gap (1.57 eV (LDA), 5.68 eV (GW$_0$)), while the chair configuration of C$_2$F does not have a band gap and still maintains metallic behavior. The calculated results made by Liu et al.\cite{18e} showed that two fluorinated graphenes (CF, C$_F$) have band gaps (3.13 eV, 2.92 eV), while others (CF$_{0.056}$, CF$_{0.031}$) are still metallic and do not open a band gap. Therefore, all of these results indicate that the band-gap opening depends mainly on the F-binding configuration, not just the adsorption level.

Effects of F-adsorption levels

As shown in Table 2, case A$_2$ with two C$_F$ defects on adjacent sites with fluorine atoms above and below the plane, has the lowest binding energy. In order to explore the binding energy change for this configuration with different F-adsorption levels, the supercell size was varied from $1 \times 1 \times 1$ to $8 \times 8 \times 1$. In this manner, the fluorine concentration was varied from 50% to 1.6%. Table 4 shows the calculated F-binding energies ($E_b$) for F-adsorption level from 50% to 1.6%. It can be seen that as the fluorine concentration decreases down to 33.3%, $E_b$ remains essentially constant. Between 33.3% and 20%, $E_b$ decreases and thereafter remains essentially constant with decreasing fluorine concentration. These results indicate that at low F-adsorption levels, there is strong bonding interaction

![Figure 10](image)

Figure 10. The total and partial density of states of 2F-adsorbed graphene case C with band-gap opening of 0.37 eV. Similar figures for the other cases are included in the Supporting Information.

### Table 4. Binding energies of different fluorine concentrations: two fluorines bonded on two adjacent carbons on opposite sides of graphene (case A2).

| No. of C | F/C ratio | F (%) | $E_b$ (eV/1 F) |
|---------|-----------|-------|---------------|
| 1x1x1   | 1/1       | 50    | -2.778        |
| 2x1x1   | 1/2       | 33.3  | -2.792        |
| 2x2x1   | 1/4       | 20    | -2.556        |
| 3x3x1   | 1/8       | 10    | -2.517        |
| 4x4x1   | 1/16      | 5.9   | -2.518        |
| 5x5x1   | 1/32      | 3.8   | -2.543        |
| 6x6x1   | 1/64      | 2.7   | -2.528        |
| 7x7x1   | 1/128     | 2     | -2.530        |
| 8x8x1   | 1/256     | 1.6   | -2.485        |

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between fluorine and C_{r} of graphene; however, the interaction between these two fluorine atoms is negligible due to a large separation distance. Such information is helpful for further development of SiC-supported graphene gas sensor technologies.

Conclusions

Graphene is a very promising electronic material in which defects may be used to control or optimize the electrical properties for a given application. The goal of this study was to better understand the effects of fluorine adsorption on graphene properties. In this study, first-principles density functional theory (DFT) with van der Waals dispersion interactions were used to explore the electronic and binding properties of fluorine interacting with graphene.

The calculated band structures and density of states showed that both graphite-2H and pure graphene have a zero band gap. In their valence bands, the s orbitals of carbon are the dominant contributors at lower energies while the p orbitals of carbon are more pronounced contributors at higher energies just below the Fermi level (E_{F}). In building up the sp^{2} hybrids, the s orbital of carbon participates to form low-lying σ bands while the p_{z} orbitals of carbon form the higher-lying π bands. For both graphite and graphene at E_{F}, the values of the density of states are very low which is in good agreement with XPS measurements and other theoretical reports.

When graphene is adsorbed with fluorine, a valence band (B_{v}) near the E_{F} is formed mainly from the p orbitals of the fluorine atoms with some small contribution from the p orbitals of the carbon atoms. These C_{r} defects cause a buckling of the graphene surface. When two fluorine atoms are bonded to the graphene to form two C_{r} defects, the configuration with the fluorine atoms located on opposite sides of the surface represents the most stable structure with the lowest binding energy. Depending on the fluorine binding sites, the B_{v} can serve as a valence band or a conduction band. Among the five cases studied, only two cases (C and D) open a 0.37 eV and 0.24 eV band gap respectively. Other cases still have zero band gaps. The obtained result indicates the band gap opening for graphene with low F-adsorption level strongly depends on the F-binding configurations, which is different from the fully or highly but partially fluorinated graphene.

The binding energy of fluorine on graphene depends on the F-adsorption level due to neighboring fluorine interactions. The results presented here show that for case A_{p} with two fluorine adatoms binding to adjacent carbons, but on opposite sides of the graphene sheet, the binding energy remains nearly constant down to about 33.3% F-adsorption, decreases as the concentration is lowered to about 20%, and remains nearly constant as the fluorine concentration is lowered to 2%. This suggests that at low F-adsorption levels, the interaction between neighboring pairs of fluorine adatoms is negligible, and the most important interaction is between the fluorine and carbon atoms in the C_{r} defect.

Experimental Section

Theoretical Methods: The calculations performed in this work were based on first-principles DFT with plane-wave basis sets and pseudo-potentials to describe the electron-ion interactions. The Vienna ab-initio simulation package (VASP) was employed to calculate the electronic structures of the graphene and F-adsorbed graphenes. In this study, all calculations were done using the projector augmented wave (PAW) pseudo-potentials and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional. The plane-wave basis sets were used with a plane-wave cutoff energy of 500 eV and a kinetic energy cutoff for augmentation charges of 644.9 eV. The gamma-centered k-point sampling grids obtained using the Monkhorst–Pack method, were 19 × 19 × 6 for the bulk graphite-2H, 39 × 39 × 1 for the graphene unit cell, and 7 × 7 × 1 for the supercell calculations. The valence electrons contain s and p orbitals for carbon and fluorine atoms. During calculations, all atoms in the cell, as well as the lattice dimensions and angles, were relaxed to the equilibrium configurations. The van der Waals interaction was calculated by the DFT-D3 method. For the band structure calculations, the symbols and coordinates of the high-symmetry points in the first Brillouin zone of the crystals were taken from Bradley and Cracknell’s definitions. The Bader atomic charges on each atom were calculated by a fast and robust algorithm.

Keywords: band-gap opening · DFT-D3 · electronic structures · fluorine adsorption · fluorine-doped graphene

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