

Yuhua Duan<sup>1\*</sup> Benjamin Chorpene<sup>1</sup>, Charter D. Stinespring<sup>2</sup>  
<sup>1</sup>National Energy Technology Laboratory, U. S. Department of Energy, Pittsburgh, PA 15236, USA  
<sup>2</sup>Chemical Engineering Department, West Virginia University, Morgantown, WV 25506, USA

## Motivation

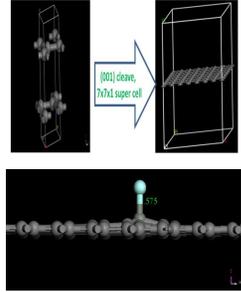
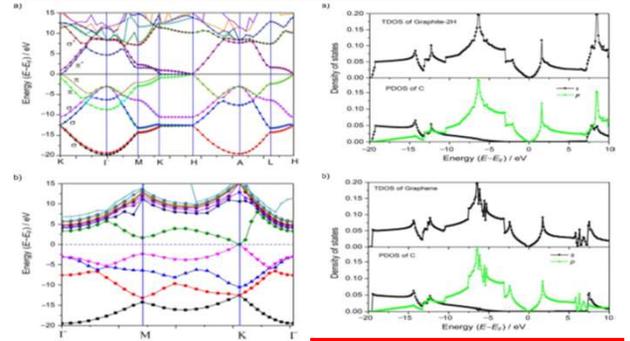
In the area of energy applications, graphene and graphene-based nanomaterials have many promising applications. Although pure graphene sheets serve as a conceptual starting point, defects, native and intentional may play a critical role in modifying and possibly optimizing graphene properties in a given application.

As a special semiconductor, graphene is a single-layer graphite sheet and acts as a zero band gap semimetal. The massless electrons in graphene with a Fermi velocity (~10<sup>6</sup> m/s) are very useful in electronic applications, such as high frequency transistors and ultrafast photodetectors.<sup>[1]</sup> However, such zero band-gap nature results in high leakage currents and power dissipation, limiting its applications.<sup>[2-6]</sup> 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 band-gap on the zero-gap of pristine graphene.<sup>[2]</sup>

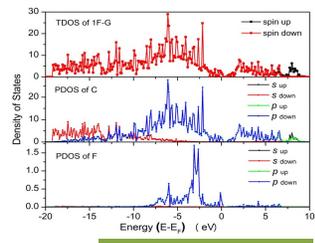
## Theoretical Approach

To better understand the effects of low-level fluorine in graphene-based sensors, first-principles density functional theory 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.<sup>[7-8]</sup>

## Band-Structure of Graphene & Graphite-2H



## 1F-doped on Graphene

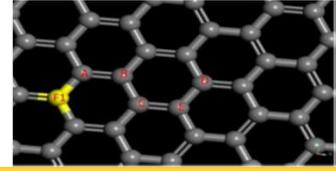


No band-gap opening

## 2F-Doped on Graphene

Table 1. The calculated binding energy ( $E_b$ ),  $C_F$  buckling off graphene plane ( $Z_{CF}$ ),  $C_F$ -F bond-length ( $r_{CF}$ ) and angle F-C<sub>1</sub>-C<sub>2</sub> in 1F- and 2F-adsorbed graphene

F on same side of G	G-1F	G-2F (case A <sub>1</sub> )	G-2F (case B <sub>1</sub> )	G-2F (case C <sub>1</sub> )	G-2F (case E <sub>1</sub> )	G-2F (case D <sub>1</sub> )
$E_b$ (eV/IF)	-2.071	-2.225	-1.913	-2.301	-1.976	-2.158
$Z_{CF}$ (Å)	0.503	0.845	0.637	0.623	0.505	0.525
$r_{CF}$ (Å)	1.575	1.462	1.553	1.495	1.589	1.528
$\angle F-C_1-C_2$ (°)	102.40	102.04	106.25	104.06	102.66	103.44



5 binding sites with 10 configurations

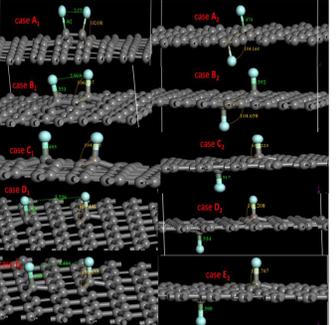
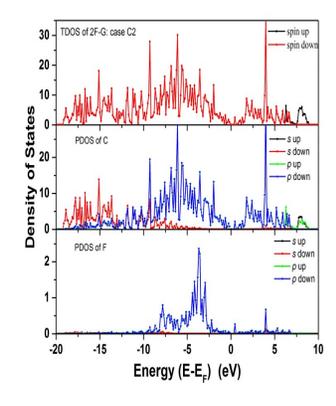
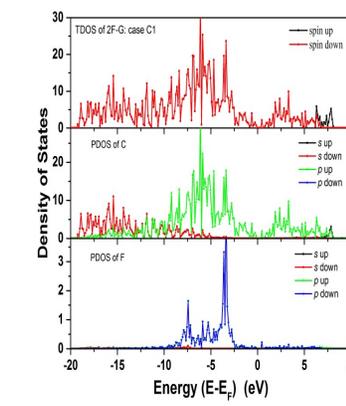


Table 2. The calculated charges on F and  $C_F$ , F-band ( $B_F$ ) width and gap between  $V_B$  and  $B_1$  ( $E_{VB-B_1}$ ) of 1F- and 2F-adsorbed Graphene (G).

F on opposite side of G	G-1F	G-2F (case A <sub>2</sub> )	G-2F (case B <sub>2</sub> )	G-2F (case C <sub>2</sub> )	G-2F (case E <sub>2</sub> )	G-2F (case D <sub>2</sub> )
$E_{VB}$ (eV)	0.119	0.371	0.352	0.478	0.144	0.240
$B_F$ width*	0.359	0.124	0.587	0.120	0.471	0.359
F charge	-0.59	-0.65	-0.57	-0.59	-0.58	-0.58
$C_F$ charge	0.33	0.55	0.39	0.51	0.49	0.48

Only some of configurations have band-gap. At low-F concentration, the band-gap opening depends not only on the F-concentration, but also on the binding configurations.

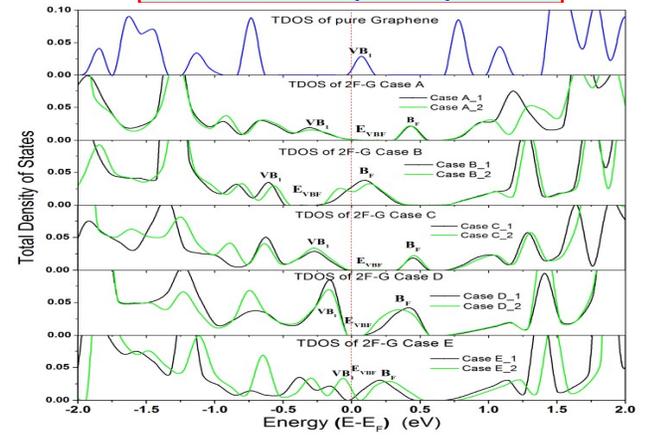


## Relationships of Binding Energy with F concentration

Table 3. Binding energies ( $E_b$ ) of different F concentrations: two F bonded on adjacent two-C opposite side of graphene (case A2).

Supercell	1x1x1	2x1x1	2x2x1	3x3x1	4x4x1	5x5x1	6x6x1	7x7x1	8x8x1
# of C	2	4	8	18	32	50	72	98	124
F/C ratio	1/1	1/2	1/4	1/9	1/16	1/25	1/36	1/49	1/62
F (%)	50	33.3	20	10	5.9	3.8	2.7	2	1.6
$E_b$ (eV/IF)	-2.778	-2.792	-2.556	-2.517	-2.518	-2.543	-2.528	-2.530	-2.485

## TDOS of 2F-doped Graphene



## Conclusions

When graphene is adsorbed with fluorine, a valence band ( $B_F$ ) 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  $C_F$  defects cause a buckling of the graphene surface. When two fluorine atoms are bonded to the graphene to form two  $C_F$  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  $B_F$  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 partial 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<sub>2</sub> 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 level, the interaction between neighboring pairs of fluorine adatoms is negligible and the most important interaction is between the fluorine and carbon atoms in the  $C_F$  defect.

Further work are focusing on the optical and band-gap opening properties of the low-F concentration binding on multi-graphene layers with/without SiC support.

## References

- V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, *et al.*, *Chem. Rev.* **2012**, *112*, 6156-6214
- L. Liao, H. L. Peng, Z. F. Liu, *J. Am. Chem. Soc.* **2014**, *136*, 12194-12200;
- V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, A. H. C. Neto, *Rev. Mod. Phys.* **2012**, *84*, 1067-1125.
- R. Paupitz, P. A. S. Autreto, S. B. Legoas, *et al.*, *Nanotechnology* **2013**, *24*, 035706
- H. Y. Liu, Z. F. Hou, C. H. Hu, Y. Yang, Z. Z. Zhu, *J. Phys. Chem. C* **2012**, *116*, 18193-18201.
- H. F. Bettinger, K. N. Kudin, G. E. Scuseria, *J. Phys. Chem. A* **2004**, *108*, 3016-3018
- Y. Duan, C. D. Stinespring, B. Chorpene, *ChemistryOpen*, **2015**, *4*, 642-650
- S. Raghavan, T. J. Denig, T. C. Nelson, C. D. Stinespring, *J. Vac. Sci. Technol. B* **2012**, *30*, 030605.