ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Electronic properties of group-IV nanosheets functionalized with hydrogen and fluorine

WenBiao Kang[1,2] and Jianbao Wu[1]
1. School of Fundamental Studies, Shanghai University of Engineering Science, Shanghai 201620, *Chin*a
2. School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

Manuscript Info

Manuscript History:

Received: 14 October 2015
Final Accepted: 25 November 2015
Published Online: December 2015

Key words:

nanosheets, electronic structures,

***Corresponding Author**

Jianbao Wu

Abstract

First-principles calculations based on density-functional theory reveal some unusual electronic properties of group-IV nanosheets functionalized with hydrogen and fluorine. According to difference in electronegativity between H and F atom, fully hydrogenation, full fluorination and codecorated with H and F are all break the symmetry of Dirac point and could tune the size of band gap. Fully fluorination generates the smallest band gap, while fully hydrogenation gain the biggest band gap. The diverse electronic properties of decorated group-IV nanosheets have the potential for wider applications of 2D-based materials and devices.

INTRODUCTION

Because of their unique properties, carbon-based low-dimensional nano-structure have been of interest to scientists for many years. Among these "graphene"[1-4], a two-dimensional planner structure that can viewed as a single layer of graphite, has been proposed as a versatile materials for many potential applications. Recently fully hydrogenated graphene, which is referred to as "graphane"[5] has been predicted theoretically and synthesized experimentally by exposing graphene in hydrogen plasma environment. More importantly, graphane is a semiconductor while graphene is a conductor. Hydrogenation of graphene is reversible, providing the flexibility to manipulate its coverage. For example, one can remove the hydrogen atoms from one side of graphane, while keeping the other side hydrogenated. This will result in a half-hydrogenated graphene which we refer to as "graphone". It is interesting to know the effect of partial hydrogen coverage on the electric structure and properties of graphene.

Investigating similar characteristics of other group-IV elements such as silicon and germanium is therefore, important and promising, since silane and germane exist alongside methane. It turns out that study of the stability of a single hexagonal sheet of Si and Ge goes back at least to 1994 paper by Takeda and Shiraishi [6] using density-functional theory (DFT) whithin the local-density opproximation (LDA). More recently, interst has grown in the study of such sheets including Group IV-IV and III-V compounds [7-9]. Just as for graphene, the culmination is, without doubt, the experimental growth of silicene nanosheets and nanoribbons. Thus, already in 2006, Nakano et al. [10] reported the synthesis of single-crystal silicon monolayer sheets via the chemical exfoliation of $GaSi_2$. In the more recent work, the Si nanoribbons were deposited on a silver substrate. For Ge, Cahangirov et al. found two local minima with buckling heights of 0.64 Å (low buckled) and 2.0 Å (high buckled) but with only the former being stable. There are other papers on the two-dimensional Ge sheet named germanene however, we note that three of them studied the flat germanene structure as if it is the stable one, hence, their usefulness is limited. Beyond the lattice properties, the electronic and phonon structures have also been studied. Thus graphene, silcene and germanene are all predicted to be zero-gap semiconductors.

of the electronic structure and magnetic of full decorated Group-IV nanosheets using H and/or F atoms. We show that fully hydrogenation, full fluorination and codecorated with H and F are all break the symmetry of Dirac point and could tune the size of band gap. Fully fluorination generates the smallest band gap, while fully hydrogenation gain the biggest band gap. The diverse properties of decorated group-IV nanosheets have the potential for wider applications of 2D-based materials and devices.

1. Method of calculation

Our calculations are based on spin-polarized density functional theory (DFT) using generalized gradient approximation (GGA) for exchange-correlation potential. We have used Perdew-Burke-Ernzerhof (PBE) functional for GGA as implemented in the Vienna ab initio Simulation Package (VASP) [12, 13]. For the geometric and electronic structure calculations, a supercell is used with a vacuum space of 15 Å between two layers to avoid interactions between them. Pseudopotentials with $2s^2sp^4$, $3s^23p^4$, $2s^22p^4$, $1s^1$, and $2s^2sp^5$ valence electron configurations, respectively, for C, Si, Ge, H, and F atom are used. The Brillouin zone is represented by Monkhorst-Pack special K- point mesh of 991. The energy cutoffs, convergence in energy, and force are set to 400 eV, 1 eV, and 0.01eV/Å, respectively. Optimizations are performed using conjugated gradient method and without any symmetric constraints. The accuracy of our calculation procedure is tested using pristine Group-IV nanosheets, the relevant structural parameters computed are given in table I. From the table I in plane hexagonal lattice constant (Δ) for graphene, two dimensional low-bulked silicon and germanium honeycomb structures are 2.46, 2.76 and 2.82 Å, the buckling height Δ for silicon and germanium honeycomb structures are 0.43 and 0.63 Å. These structures parameters are in good agreement with theoretical result calculated by S. Cahangirov et al. The calculated electronic band structures (BS) for graphene, two dimensional low-bulked silicon and germanium honeycomb structures are presented in Fig-1, where the band structures of Si and Ge show behaviors similar to graphene, π and π^* bands for 2D low-buckled honeycomb structures of Si and Ge crossing at K- and K-* points at E_F are semimetallic.

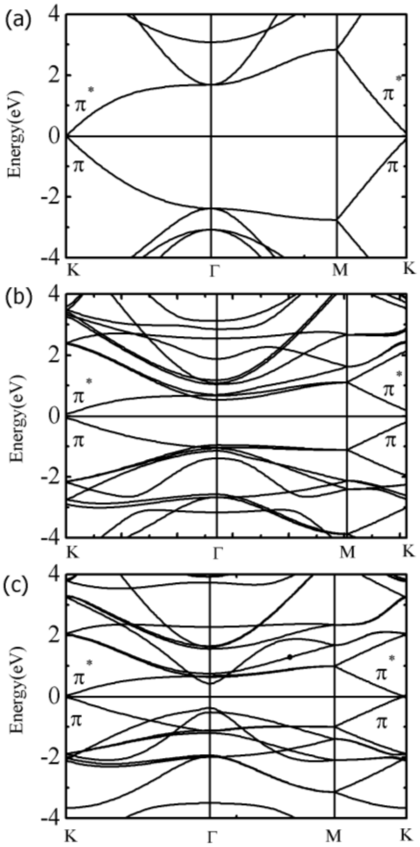

Fig-1. The band structures for pristine group-IV nanosheets. (a) for graphene; (b) for silicene (c) for germanene.

2. Results and discussions

In the following, we discuss the electronic structure and properties of Group-IV nanosheets when (A) fully hydrogenated, (B) fully fluorinated, (c) codecorated with H and F.

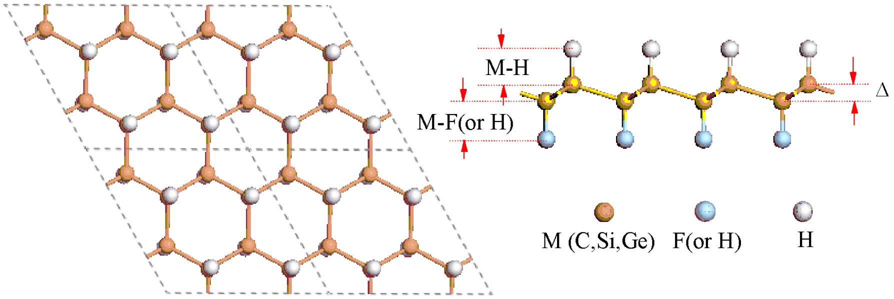

Fig-2. The schematic diagram of group-IV nanosheets decorated with H and F atoms. Left panel and right panel represents top view and side view. Purple spheres are group-IV (C, Si, Ge) atoms, white for H atoms, and blue for F atom but also stand for F atoms when system fully hydrogenated.

2.1 Fully hydrogenated group-IV nanosheets

Following the idea of hydrogenated of graphene sheet, we first discuss the results for fully hydrogenated group-IV nanosheets. Most of the relevant structural parameters computed are given in Table I, where is in plane hexagonal lattice constant and is the buckling height. It was found that all the structures were buckled as shown in Fig-2, particularly, the buckling height of graphene is 0.00 Å, when fully hydrogenated graphene the buckling height increase to 0.46 Å, the buckling height of two dimensional Si and Ge also have a increase of 0.29 Å and 0.10 Å respectively. In the fully hydrogenated group-IV nanosheets structures M(C, Si, Ge) atoms become hybridized which distorts the plannar geometry forming a zigzag configuration with distance found to be 0.46, 0.72, and 0.73 Å. Compared to pristine group-IV nanosheets introducing H atoms make the value of in plane hexagonal lattice constant α increased by 0.07, 0.08, and 0.26 Å for C, Si, and Ge respectively. Hydrogen atoms are adsorbed on the top site of M atoms, the bond length of C-H is 1.11 Å, that of Si-H is 1.50 Å, and that of Ge-H is 1.56 Å. To study the energetics of hydrogenation, we calculated the formation energy which is defined as the energy difference between the hydrogenated group-IV nanosheets, pristine group-IV nanosheets, and H_{2} molecules. We found thatin contrast to the graphene sheet, the hydrogenation of silicene and germanene are endothermic with energy of 0.195 and 0.187 eV/H.

Table 1. Structural parameters of pristine, fully hydrogenated, full fluorinated and group-IV nanosheets decorated with H or F. (Å) and (Å) stand for in plane hexagonal lattice constant and the buckling height, which both indicated in Figure 1. M-H (Å) are the M (C, Si, Ge)-H bond lengths M-F (Å) are the M (C, Si, Ge)-F bond lengths (eV) stand for energy-band gap.

	pure nanosheets			**fully hydrogenated**			**full fluorinated**			**decorated with H or F**		
	C	**Si**	**Ge**	**C**	**Si**	**Ge**	**C**	**Si**	**Ge**	**C**	**Si**	**Ge**
(Å)	2.46	2.76	2.82	2.53	3.88	4.08	2.52	3.88	4.14	2.55	3.87	4.19
(Å)	0.00	0.43	0.63	0.46	0.72	0.73	0.48	0.72	0.60	0.47	0.72	0.68
M-H (Å)	-	-	-	1.11	1.50	1.56	-	-	-	1.10	1.50	1.56
M-F (Å)	-	-	-	-	-	-	1.35	1.52	1.79	1.39	1.63	1.79
(eV)	0.00	0.00	0.00	3.75	2.14	0.99	2.71	0.62	0.32	3.30	1.65	0.70

The energy-band structures for H-M-H are plotted in Fig-3. It is found to be nonmagnetic with a direct band gap of 3.75, 2.14, and 0.99 eV for H-C-H, H-Si-H, and H-Ge-H, respectively. The valence-band maximum (VBM) and conduction-band minimum (CBM) are both located at the Γ point in the reciprocal space. Unlike the pristine group-IV nanosheets that are semimetallic, for the fully hydrogenated group-IV nanosheets, introducing H atoms break the symmetry of Dirac point and open a direct band gap.

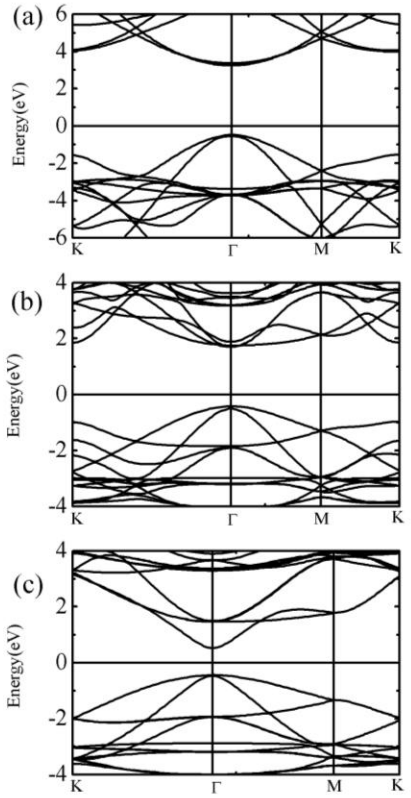

Fig-3. The band structures for Fully hydrogenated group-IV nanosheets. (a) for graphene; (b) for silicene; (c) for germanene.

2.2 Fully fluorinated group-IV nanosheets

As stated in previous discussions, fully hydrogenation could make group-IV nanosheets more bulked and open a direct band gap. We now discuss the results for fully fluorinated group-IV nanosheets. Most of the relevant structural parameters computed are given in Table I, from the table I fully fluorination make these in plan hexagonal lattice constants of group-IV nanosheets increased a little when compared to fully hydrogenation. Fully fluorination also distorts the group-IV nanosheets, as shown in Fig-2. the buckling height of the fully fluorinated graphene and two dimensional honeycomb Si is 0.48 and 0.72 Å, but for the two dimensional honeycomb Ge the buckling height is only 0.60 Å, so fully hydrogenation could distort the nanosheets of Ge more than fully fluorination. Atoms of F are adsorbed on the top site of M atoms, the bond length of C-F is 1.35 Å, that of Si-F is 1.52 Å, and that of Ge-F is 1.79Å.

The energy-band structures of H-M-H are plotted in Fig-4. It is found to be nonmagnetic with a direct band gap of 2.71, 0.62, and 0.32 eV for F-C-F, F-Si-F, and F-Ge-F, respectively. For nanosheets of group-IV elements introducing F atoms also break the symmetry of Dirac point but open a smaller direct band gap by compared with introducing H atoms, for the reason, lies in that the length of M-F is larger than that of M-H, and the electronegativity of F atom are much larger than that of H atom.

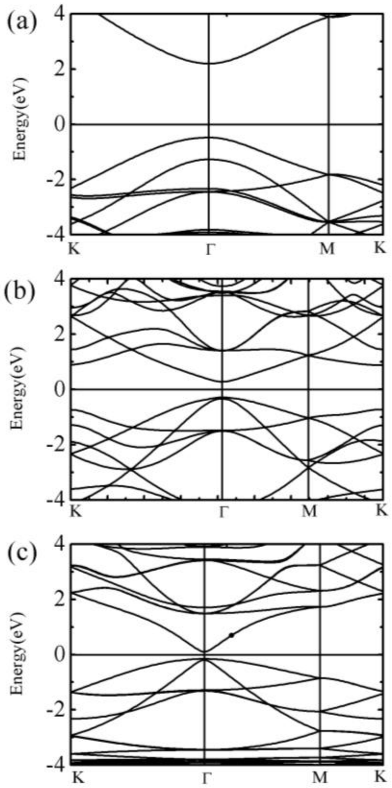

Fig-4. The band structures for Fully fluorinated group-IV nanosheets. (a) for graphene (b) for silicene (c) for germanene.

2.3 Group-IV nanosheets codecorated with H and F

As we have seen from above that both fully hydrogenation and fully fluorination could break the symmetry of Dirac point of graphene, Low-bulked honeycomb structures of Si and Ge with more distort the nanosheets. In this section, we discuss the effect of introducing the H atom and F atom in the group-IV nanosheets at the same time forming three type of codecorated sheet. For these the H atom and F atom codecorated sheet, F atoms are attached to one M (C, Si, Ge) site while H atoms are attached to the other M site (labeled F-M-H, as shown in Fig-2). After fully optimized the length of bonds of M-F and M-H in F-M-H systems are the same as the length of that in fully hydrogenated systems and fully fluorinated systems, which can been seen in table 1.

The energy-band structures of F-M-H are plotted in Fig-5. It is found to be nonmagnetic with a direct band gap of 3.30, 1.65, and 0.70 eV for F-C-H, F-Si-H, and F-Ge-H, respectively. For nanosheets of group-IV elements introducing F and H atoms at the same time, which also break the symmetry of Dirac point and open direct band gap. As seen in table 1, the band gap of F-M-H is lager than that of F-M-F but smaller than that of H-M-F. In view of difference in electronegativity between H and F atom, codecorated gourp-IV nanosheets with H and F could tune the band gap by break the symmetry of Dirac point.

Conclusion

In conclusion, we have performed first-principle pseudo-potential calculations on the electric property of group-IV nanosheets decorated with hydrogen and fluorine. According to difference in electronegativity between H and F atom, fully hydrogenation, full fluorination and codecorated with H and F are all break the symmetry of Dirac point and could tune the size of band gap. Fully fluorination generates the smallest band gap, while fully hydrogenation gain the biggest band gap. The diverse properties of decorated group-IV nanosheets have the potential for wider applications of 2D-based materials and devices.

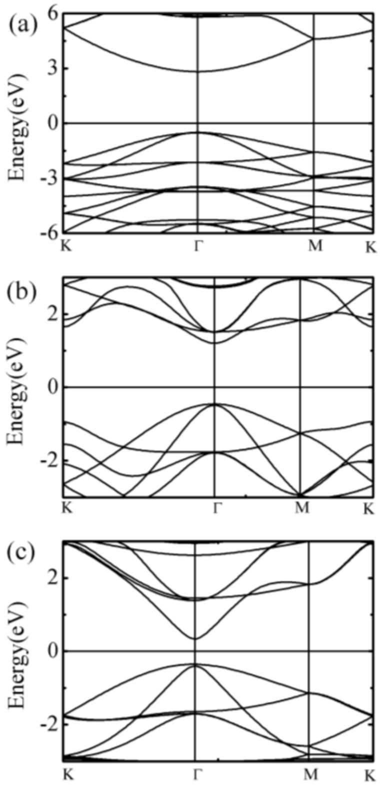

Fig-5. The band structures for Group-IV nanosheets codecorated with H and F. (a) for graphene (b) for silicene (c) for germanene.

References

1. Geim, A. K. Novoselov, K. S. *Nat.Mater.* ***6***, 183 (2007).
2. C. Berger, Z. Song,Li, X. Wu, X. Brown, N. Naud, C. Mayou, D. Li, T. Hass, J. Marchenkov, A. N. Conrad, E. H. First, P. N. de Heer, *Science*, ***312,*** 1191. (2006).
3. Y. Jiang, Z. Small, J. P. Purewal, M. S. Tan, Y.-W. Fazlollahi, M. Chudow, J. D. aszczak, J. A. tormer, H. L. Kim, P.. *Phys. Rev. Lett.*, ***96,*** 136806 (2006).
4. K. S. Geim, A. K. Morozov, S. V. Jiang, D. Katsnelson, M. I. Grigorieva, I. V. Dubonos, S. V. Firsov, *Nature*, ***438,*** 197. (2005)
5. J. O. Sofo, A. S. Chaudhari, and G. D. Barber, *Phys. Rev. B* **75,** 153401 (2007)
6. K. Takeda and K. Siraishi, *Phys. Rev. B*, **50**, 14916 (1994).
7. S. Cahangirov, M. Topskal, E. Akturk, H.Sahin, and S. Ciraci, *Phys. Rev. Lett.*, **102**, 236804 (2009)
8. Y. Ding and J.Ni, *Applied Physics Letters*, **95**, 08315 (2009).
9. A. Lu, X. Yang, and R. Zhang, *Solid State Communi.* **149**, 153 (2009).
10. H. Nakano, T. Mitsuoka, M. Harda, K. Horibuchi, H. Nozaki, N. Takahashi, T. Nonaka, Y.Seno, and H. Nakamura, *Angew. Chem.*, **118,** 6451 (2006).
11. G. Kresse, J. Furthmuller, *Phys. Rev. B* **54** 11169 (1996).
12. Y. Sugimoto, M. Abe, S. Hirayama, N. Oyabu, O. Custance, and S. Morita, *Nature Materials*, **4** 156. (2005)