Effect of normal strain and external electric field on electronic properties of the GeC bilayer: A first-principles study

Luo Min, Xu Yu E, and Shen Yu Hao
Effect of normal strain and external electric field on electronic properties of the GeC bilayer: A first-principles study

Cite as: AIP Advances 9, 125324 (2019); doi: 10.1063/1.5109686
Submitted: 10 May 2019 • Accepted: 28 November 2019 • Published Online: 23 December 2019

Luo Min, Xu Yu E, and Shen Yu Hao

AFFILIATIONS
1 Department of Physics, Shanghai Polytechnic University, Shanghai 201209, China
2 Department of Electronic Engineering, Shanghai Jian Qiao University, Shanghai 201306, China
3 Key Laboratory of Polar Materials and Devices, East China Normal University, Shanghai 200241, China

ABSTRACT

The electronic properties of the GeC bilayer with different stacking patterns are investigated using density functional theory. A different behavior shows up when applying normal strain and electric field (E-field). Under normal strain, the bandgap becomes very elastic and presents an indirect-to-direct bandgap transition. By applying the E-field, the intrinsic bandgap swiftly reduces to zero. The major modulation of the bandgap is mainly due to the migration of Ge-p orbitals in the conduction band. Our results reveal the flexible electronic properties of the GeC bilayer, which would provide a theoretical reference for the development of the GeC bilayer.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5109686

I. INTRODUCTION

Novel functional two-dimensional (2D) materials with unique and unpredictable features have become a hot topic in recent years. Typically, the discovery of graphene has gained much interest owing to its excellent physics and potential applications in nanoelectric devices. However, graphene is a zero-bandgap semiconductor, which limits its applications in nanodevices and integrated circuits. As is well known, the bandgap near the Fermi energy is critical for controlling electron conductivity. All these years, many studies focused on searching for other new 2D materials. Recently, except for graphene, research interests have been extended to other similar materials. A large number of new 2D materials, such as single-layer MoS$_2$ and h-BN, have been found, which display excellent mechanical, thermoelectric, optical, and electronic properties.

Very recently, much research was carried out on the tunable bandgap of 2D materials. New 2D materials, such as G/BN, G/MoS$_2$, G/SiC, consisting of similar atomic structures have been found, which has prompted intensive studies. The crucial factor for controlling the bandgap of 2D semiconductor materials is the existence of new electronic and optical properties that make the application of these 2D materials in nanoelectronic devices achievable. Currently, many reports have testified that applying strain or electric field (E-field) should be an effective method for tuning the electronic properties of 2D materials. Moreover, group-IV compounds, such as monolayer GeC, have attracted some attention due to their large bandgap of 2.1 eV. Many studies have been performed to optimize their electrical properties by absorption, impurities, and defects. To the best of our knowledge, studies on the tunable electronic properties of the GeC monolayer under strain and E-field, which would result in a performance different from that of the intrinsic GeC monolayer, are still lacking.

In this work, we have systematically studied the electronic properties of the GeC bilayer by the density functional theory (DFT) method. We considered a total of four stacking patterns. At equilibrium, we demonstrate that the four patterns exhibit a direct bandgap of 2.06, 2.02, 1.83, and 1.65 eV, respectively. Under normal strain, the bandgaps could be modified elastically, ranging from 0 to 2.16 eV. By applying an E-field, the bandgap in...
these systems monotonously decreases to 0 eV. It is found not only that the values of bandgaps could be regulated but also that their components could be modified. The tunable bandgap of the current system will make it a promising candidate in nanoelectronic devices.

II. COMPUTATIONAL METHODS

All the works are performed by using the VASP computer program\(^3\) with the projector-augmented wave method. We use the generalized gradient approximation (GGA) exchange correlation with Perdew-Burke-Ernzerhof (PBE) function.\(^3\) A mesh of \(10 \times 10 \times 1\) k-points is used. The expansion of plane-wave functions is set up to a cutoff energy of 450 eV. In our case, the GeC bilayer consists of a \(2 \times 2 \times 1\) GeC supercell. The lattice constant of pristine GeC is set at 3.23 Å. To describe the van der Waals (vdW) interaction, we use the DFT-D2 method with Grimme vdW correction.\(^4\) The vacuum is set to 20 Å. All structures are fully optimized until the residual force is smaller than 0.01 eV/Å, and the convergence of total energy is set to \(1.0 \times 10^{-6}\) eV/atom.

III. RESULTS AND DISCUSSIONS

A. Electronic properties of the GeC bilayer under normal strain

First of all, as illustrated in Fig. 1, four different stacking patterns, namely, AA, AA’, AB, and AB’, of the GeC bilayer are considered for our calculations. In AA-stacking, the top and the bottom GeC layer directly stack along the c-axis [Fig. 1(a)]. In AA’ stacking, the germanium and carbon atoms exchange their positions in the top layer [Fig. 1(b)]. In AB stacking, the top layer and the bottom layer have a dislocation, where the carbon atoms of the top layer align with the germanium atoms of the bottom GeC layer [Fig. 1(c)]. In AB’ stacking, the top layer and the bottom layer look like mirror images [Fig. 1(d)]. As we know, the current bilayer is composed of two GeC monolayers; hence, it is difficult to achieve bilayer stability. In order to solve this problem, we calculate the binding energies of...
FIG. 4. Band structures of (a) AA, (b) AA′, (c) AB, and (d) AB′ stackings with different interlayer distances. The Fermi levels are marked by dashed lines.
different stackings, which are defined as
\[ E_b = E_T - (E_{\text{top}} + E_{\text{bottom}}), \]

where \( E_T \) is the total energy of the bilayer and \( E_{\text{top}} \) and \( E_{\text{bottom}} \) are the total energies of the top and the bottom GeC monolayers, respectively. Previous studies have verified that it was easy to apply normal strain to the vdW heterostructures. \(^{35-37} \) Hence, the normal strain along the c-axis can be evaluated by the interlayer distance (d) between two GeC layers [see Fig. 1(a)]. After we fully optimize the structures, the binding energy as a function of the interlayer distance is given in Fig. 2.

From Fig. 2, it can be seen that the calculated binding energies change along with the interlayer distance (d). On the basis of the calculated binding energies, the stable states of the different stacking patterns are quite different. As shown in Fig. 2, the AA, AA′, AB, and AB′ stacking get a lowest value of \(-0.020, -0.088, -0.099, \) and \(-0.056 \text{ eV}, \) and the equilibrium distance (d\(_0\)) of these four stacking structures is about \(6.0, 3.8, 3.8, \) and \(4.0 \text{ Å}, \) respectively. Moreover, the corresponding bandgap at their equilibrium states is approximately \(2.06, 2.02, 1.83, \) and \(1.65 \text{ eV}, \) Here, while the distance is smaller than d\(_0\), compressive strain is applied and vice versa. As shown in Fig. 3, under normal strain, the overall variation of the bandgap for the AA′ stacking is very limited, changing from 1.91 to 2.11 \text{ eV}. For the AA stacking, the bandgap is almost the same under tensile strain, changing from 2.09 to 2.11 \text{ eV}. For the AB and the AB′ stacking, the growth of the bandgap is also very moderate while tensile strain is applied. However, with compressive strain, for the AA, AB, and AB′ stacking, the bandgap shrinks monotonously, ranging from 2.06 to 0 \text{ eV}, 1.83 to 1.32 \text{ eV}, and 1.65 to 0.06 \text{ eV}, respectively. Based on the analysis of Fig. 2, compressive strain has a large impact on the variation of the bandgap.

In order to better understand the electronic properties of the GeC bilayer under normal strain, band structures around the Fermi level (\( E_F \)) with different interlayer distances are calculated, as shown in Fig. 4. Analyzing from Figs. 4(a) and 4(c), under normal strain, the variations of bandgaps mainly attribute to the shift in the conduction band (CB) and have no concern with the valence band (VB). However, the details of the variations are different. For the AA and the AB stacking, a direct bandgap always appears, the system always shows a direct bandgap, and the CB moves far from \( E_F \) along the K-point. For the AA′ and the AB′ stacking, the systems show direct-indirect transitions by applying compressive strain, but the systems maintain direct bandgaps under tensile strain. Our results indicate that normal strain not only regulates the value of the bandgap but also regulates its component. In this paper, to verify whether normal strain could be achieved in the real situation, we calculate compressive strain, which can be estimated as \( \varepsilon = (E-E_0)/[A(d-d_0)], \) where \( E \) and \( E_0 \) are the total energies of the systems under strain and without any strain and \( A \) is the area of the supercell. \(^{29} \) At \( d = 2.7 \text{ Å}, \) the maximum compressive strain upon four stacking structures is about 8.2 GPa. In the previous work, a much larger compressive strain (\( \sim 35 \text{ GP} \)) has been achieved experimentally. \(^{33} \) The current value is much smaller and could be realized in the experiment.

**B. Tuning the bandgap by the electric field**

We now examine the electronic structure of the GeC bilayer under an electric field (E-field). Here, the strength of the E-field ranging from 0 to 0.6 V/Å would not cause geometric distortion but induces charge redistribution in the systems. \(^{39,41} \) The direction of the E-field (\( \varepsilon \)) is from the bottom layer to the top layer. Variations in the bandgap with the E-field are presented in Fig. 5. For the GeC bilayer, the bandgap decreases as the strength of the E-field changes. An approximate monotonous tendency appears between the bandgap and \( \varepsilon \) in our calculations. The bandgap sharply reduces to 0 \text{ eV} while the E-field is applied. Our results reveal that the E-field could adjust the bandgap of the system effectively.

Figure 6 shows the band structures near the Fermi energy (\( E_F \)) of the GeC bilayer under different E-fields. Under an E-field, the performances of the CB and VB are a bit different. From Figs. 6(a)–6(d), under a small E-field, the whole CB moves close to \( E_F \). Interestingly, no change is found at the top of the VB. As the strength of the E-field increases, the whole VB ultimately crosses \( E_F \), which reduces the bandgap, and then it disappears. Moreover, for the four stacking structures, their endurance to the electric field is different. For the AA and the AB′ stacking, the bandgaps disappear at \( \varepsilon = 0.4 \text{ V/Å} \). For the AA′ stacking, the bandgap disappears at \( \varepsilon = 0.6 \text{ V/Å} \), while the bandgap of the AB stacking disappears at \( \varepsilon = 0.5 \text{ V/Å} \). To understand what happens in the band structure, we plot the partial densities of states (PDOS), as shown in Fig. 7. From Fig. 7, we can see that the modulations of bandgaps come from a variety of different atomic orbits of C and Ge. Figures 7(a)–7(d) show the states at the bottom of the CB are mainly dominated by the C p-orbits and partly by the Ge p-orbits and states at the top of the VB are mainly dominated by the Ge p-orbits. Under the impact of \( \varepsilon \), the p-orbits of Ge contribute to the modulations at the bottom of CB, which definitively induces the increasing variations of the bandgap.

Finally, we would like to point out that conventional DFT methods underestimate the bandgap of semiconductors. \(^{42} \) However, DFT methods are good at predicting correct trends and physical mechanisms. Thus, the qualitative trends of our results...
FIG. 6. Band structures of (a) AA, (b) AA', (c) AB, and (d) AB' stackings under different E-fields. The Fermi levels are marked by dashed lines.
FIG. 7. PDOS of (a) AA, (b) AA', (c) AB, and (d) AB' stackings under different E-fields. The Fermi level is marked by dashed lines.

seem to be correct, but the exact value of the bandgap may be hardly comparable with the experimental data. Our calculations may provide useful insight into the electronic engineering of this nanocomposite.

IV. CONCLUSIONS

In summary, we systematically investigated the electronic properties of the GeC bilayer with different stacking patterns by using
the first-principles method. In their natural states, all four of these stacking structures are direct bandgap semiconductors. Application of normal strain and E-field is found to modulate the bandgap of the GeC bilayer, but different phenomena appear. The bandgap gradually reduces as the compressive strain increases, but it becomes a little larger under tensile strain. It seems that compressive strain has greater influence on the bandgap of the GeC bilayer. By contrast, the bandgap of these four structures reduces to zero monotonously when applying an E-field. On the basis of the PDOS, such material alterations for bandgaps are due to the migrations of different atomic orbits of C and Ge. Our studies indicate that the GeC bilayer shows a widely tunable bandgap and the component of the bandgap could be changed, which can be helpful for evaluating the performance of GeC-based electronic devices.

ACKNOWLEDGMENTS

The work was supported by the Discipline Project of Shanghai Polytechnic University (Grant No. XKKZD1605), the Foundation of Shanghai Polytechnic University (Grant No. EGD18XQD29), and the Natural Science Foundation of Shanghai (Grant No. 19ZR1419800). Our work is also supported by the Research Center of Opto-Electrical Sensing, the Research Center of Resource Recycling Science and Engineering, Shanghai Polytechnic University, and the Gaoyuan Discipline of Shanghai-Environmental Science and Engineering (Resource Recycling Science and Engineering). Shanghai Polytechnic University, (Grant No. XXKZD1605), the Foundation of Shanghai Polytechnic University (Grant No. EGD18XQD29), and the Natural Science Foundation of Shanghai (Grant No. 19ZR1419800). Our work is also supported by the Research Center of Opto-Electrical Sensing, the Research Center of Resource Recycling Science and Engineering, Shanghai Polytechnic University, and the Gaoyuan Discipline of Shanghai-Environmental Science and Engineering (Resource Recycling Science and Engineering).

REFERENCES

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
2. A. K. Geim and K. S. Novoselov, Nat. Mater. 6, 183 (2007).
3. A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. 81, 109 (2009).
4. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, Nat. Nanotechnology 6, 147 (2011).
5. L. Chen, Q. Ma, H. B. Jing, H. Y. Cui, Y. Liu, and T. J. Cui, Phys. Rev. Appl. 11, 054051 (2019).
6. A. S. Rodin, A. Carvalho, and A. H. C. Neto, Phys. Rev. Lett. 112, 176801 (2014).
7. T. Low, A. S. Rodin, A. Carvalho, Y. Jiang, H. Wang, F. Xia, and A. H. C. Neto, Phys. Rev. B 90, 075434 (2014).
8. R. Fei, A. Faghaninia, R. Soklaski, J. A. Yan, C. Lo, and L. Yang, Nano Lett. 14, 6593 (2014).
9. A. Ramasubramaniam and A. R. Munir, Phys. Rev. B 90, 085424 (2014).
10. Q. Ji, X. Li, X. Qian, and J. Feng, Appl. Phys. Lett. 102, 173112 (2013).
11. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nat. Nanotechnology 7, 699 (2012).
12. M. Xu, T. Liang, M. Shi, and H. Chen, Chem. Rev. 113, 3766 (2013).
13. A. Woesner, M. B. Lundeberg, Y. Gao, A. Principi, P. Alonso-Gonzalez, M. Carrega, K. Watanabe, T. Taniguchi, G. Vignale, M. Polini, J. Hone, R. Hillenbrand, and F. H. L. Koppens, Nat. Mater. 14, 421 (2015).
14. C. H. Zhang, C. H. Jin, A. L. Koh, Y. Zhou, W. G. Xu, Q. C. Li, Q. H. Xiong, H. L. Peng, and Z. F. Liu, Nat. Commun. 6, 6519 (2015).
15. M. Yankowitz, S. Larentis, K. Kim, J. Xue, D. McKenzie, S. Huang, M. Paggen, M. N. Ali, R. J. Cava, E. Tutch, and B. J. LeRoy, Nano Lett. 15, 1925 (2015).
16. M. Li, J. C. Zhang, X. J. Hu, and Y. N. Yue, Appl. Phys. A 119, 415 (2015).
17. V. M. Pereira and A. H. C. Neto, Phys. Rev. Lett. 103, 046801 (2009).
18. S. Nigam, S. K. Gupta, C. Majumdar, and R. Pandey, Phys. Chem. Chem. Phys. 17, 11324 (2015).
19. C. X. Xia, B. Xue, T. X. Wang, Y. T. Peng, and Y. Jia, Appl. Phys. Lett. 107, 193107 (2015).
20. M. Luo, Y. H. Shen, and T. L. Yin, AIP Adv. 6, 085112 (2016).
21. H. C. Hseueh, G. Y. Guo, and S. G. Louie, Phys. Rev. B 84, 085404 (2011).
22. H. Li, R. Zhou, and X. C. Zeng, Nanoscale 6, 11685 (2014).
23. M. Luo, Y. E. Xu, and Y. X. Song, JETP Lett. 106, 46 (2017).
24. M. Luo, Y. E. Xu, and Y. X. Song, AIP Adv. 7, 015116 (2017).
25. Y. C. Rao, S. Yu, and X. M. Duan, Phys. Chem. Chem. Phys. 19, 17250 (2017).
26. Z. Xu, Y. P. Li, C. X. Li, and Z. T. Liu, Appl. Surf. Sci. 367, 19 (2016).
27. S. Majidi, S. M. Elahi, A. Esmailian, and F. Kanjouri, Prot. Met. Phys. Chem. Surf. 53, 773 (2017).
28. Z. Xu, Y. P. Li, and Z. T. Liu, J. Magn. Magn. Mater. 433, 53 (2017).
29. A. G. Gökte and E. Aktürk, Appl. Surf. Sci. 332, 147 (2015).
30. E. Ersan, A. G. Gökte, and E. Aktürk, Appl. Surf. Sci. 389, 1 (2016).
31. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
32. G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
33. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
34. S. Grimme, J. Comput. Chem. 27, 1877 (2006).
35. W. Ju, T. Li, H. Wang, Y. Yong, and X. Li, Comput. Mater. Sci. 109, 20 (2015).
36. L. Hu, J. Zhao, and J. Yang, Nanoscale 7, 8962 (2015).
37. A. P. Nayak, S. Bhattacharyya, J. Zhu, J. Liu, X. Wu, T. Pandey, C. Jin, A. K. Singh, D. Akinwande, and J. F. Lin, Nat. Commun. 5, 3731 (2014).
38. A. Manjanath, A. Samanta, T. Pandey, and A. K. Singh, Nanotechnology 26, 025701 (2015).
39. A. P. Nayak, Z. Yuan, B. Cao, J. Liu, J. Wu, S. T. Moran, T. Li, D. Akinwande, C. Jin, and J. F. Lin, ACS Nano 9, 4117 (2015).
40. Z. Ni, Q. Liu, K. Tang, J. Zheng, J. Zhou, R. Qin, Z. Gao, D. Yu, and J. Lu, Nano Lett. 12, 113 (2012).
41. N. D. Drummond, V. Zolyomi, and V. I. Falko, Phys. Rev. B 85, 075423 (2012).
42. J. Heyd, J. E. Peralta, G. E. Scuseria, and R. L. Martin, J. Chem. Phys. 123, 174101 (2005).