Chemical Functionalization of Pentagermanene Leads to Stabilization and Tunable Electronic Properties by External Tensile Strain

Jun Zhao†‡§ and Hui Zeng*†‡∥

†School of Science, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu 210023, China
‡School of Physics and Optoelectronic Engineering, Yangtze University, Jingzhou, Hubei 434023, China
§School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, China
∥Collaborative Innovation Center of Advanced Microstructures, School of Physics, Nanjing University, Nanjing, Jiangsu 210093, China

Supporting Information

ABSTRACT: Inspired by the unique geometry and novel properties of a newly proposed two-dimensional (2D) carbon allotrope called pentagraphene, we have performed first-principles calculations to study the structural stability and electronic properties of pentagermanene (pGe) modulated by chemical functionalization and biaxial tensile strain. It is observed that the 2D pGe is energetically unfavorable. However, the 2D pentagonal nanosheets can be stabilized by both hydrogenation and fluorination. Phonon dispersion spectrum and ab initio molecular dynamics simulations demonstrated that the dynamic and thermal stabilities of the two functionalized pGe nanostructures can be maintained even under a high temperature of 500 K. Our calculations revealed that both hydrogenated and fluorinated-pentagonal germanenes are semiconductors with indirect band gaps of 1.92 and 1.39 eV (2.60 and 2.09 eV by the hybrid functional), respectively. The electronic structures of the functionalized pGes can be effectively modulated by biaxial tensile strain, and an indirect to direct gap transition can be achieved for the hydrogenated pGe sheet by 6% biaxial strain. Moreover, the band gap of the hydrogenated pGe could be further tailored from 0.71 to 3.46 eV (1.16−4.35 eV by the hybrid functional) by heteroatom doping (C/Si/Sn/Pb), suggesting the semiconductor−insulator transition for differently doped nanostructures. As a result, the functionalized pGes are expected to have promising applications in nanoelectronics and nanomechanics.

INTRODUCTION

Graphene, presenting exceptional properties derived from the truly two-dimensional (2D) nanostructure, has rapidly and continually attracted enormous interests of researchers in various disciplines since its fabrication in 2004.1 Inspired by the exotic properties originating from the 2D nanostructure, group-IV (silicon, germanium, and tin) analogues have been theoretically and experimentally investigated.2,3 The 2D silicene, germanene, and stannum sheets with low-buckled structures are predicted to be stable at first through first-principles calculations,4−6 and then they have been experimentally fabricated on a metal surface7−12 Furthermore, the characterized electronic properties of the group-IV analogues in experiments are in good agreement with the computational modeling reported previously. It is noticed that most inorganic nanosheets possess hexagonal lattices similar to those of graphene, such as binary BN nanosheets with flat honeycomb13 and transition-metal dichalcogenides (MoS2, WS2, and MoSe2) with buckled honeycomb.14,15 In addition, the recently fabricated black-phosphorene nanosheets with puckered nanostructure can also be regarded as akin to hexagonal lattices.16,17

More recently, a new 2D carbon allotrope named pentagraphene, presenting a tetragonal lattice with threefold and fourfold coordinated hybrid carbon sheets, was proposed by computational modeling.18 The pristine pentagraphene is found to have negative Poisson’s ratio, ultrahigh strength, and reduced thermal conductivity compared to those of graphene.19 More importantly, first-principles calculations have revealed that pentagraphene is a semiconductor with a quasidirect band gap of 3.25 eV, suggesting that it could be a promising candidate for possible applications in the field of nanoelectronics and optoelectronics.20,21 In addition, some pentagraphene-like analogues have also been proposed and predicted to be stable at room temperature.22−24 Meanwhile, surface decoration can be utilized to improve the stability, electronic
structure, and thermal conductivity of 2D nanomaterials.\textsuperscript{25−28} Previous studies have shown that the energetic and mechanical stabilities of pentasilicene can be greatly improved via hydrogenation,\textsuperscript{29} the electronic and mechanical properties of pentagraphene can also be effectively modulated by hydrogenation and fluorination,\textsuperscript{30} and unexpected enhancement in the thermal conductivity can be obtained for the hydrogenated pentagraphene.\textsuperscript{31}

Recently, Goldberger’s research group has fabricated freestanding monolayers of hydrogenated germanium (GeH) and methylated germanium (GeCH\(_3\)) by a chemical method, and their characterizations on these monolayer germananes have shown that they have large direct band gaps and high electron mobilities.\textsuperscript{32−34} More importantly, previous studies have shown that the structural stability, electronic structure, and transport properties of Ge-based 2D nanomaterials can be improved by covalent chemistry decoration of different surface ligands,\textsuperscript{35−38} allowing us to tailor desirable properties to achieve practical applications in the fields of electronics and optoelectronics.\textsuperscript{39−42}

Motivated by the advance of chemically functionalized Ge-based 2D nanomaterials and the penta structure with tetragonal lattice, researchers would wonder the possibility of experimental realization of pentagermanene (pGe) and the influences of chemical functionalization on the stability and electronic structures of pGe. Thus, in this article, we have carried out first-principles calculations to study the structural stability of pristine pGes and chemically functionalized pGes by analyzing the phonon dispersion and adsorption energy. It is found that pristine pGe is dynamically unstable; however, the Ge-based pentagonal structure can be stabilized by hydrogenation and fluorination. Furthermore, the influences of biaxial strain on the electronic properties of hydrogenated and fluorinated pGes have been investigated in detail. The band gap of the hydrogenated pGe could be further tailored by heteroatom doping (C/Si/Sn/Pb). Our results could be helpful in understanding the electronic properties of Ge-based nanomaterials and may be useful for the development of Ge-based electronics.

### RESULTS AND DISCUSSION

Figure 1a shows the atomic structural geometry of pristine pGe, presenting a tetragonal lattice consisting of four pentagons in the primitive cell. The optimized lattice constant of the pristine pGe is \(a = 5.668\, \text{Å}\), and the structure possesses the \(P\bar{4}2_1\)m symmetry (space group no. 113). The unit cell comprises two tetracoordinated Ge atoms and four tricoordinated Ge atoms, and for convenience, they are labeled as Ge1 and Ge2, respectively. Furthermore, we label the pristine pGe as pGe in the following discussions. For the pGe nanostructure, the bond length of Ge1–Ge2 atoms is \(R_1 = 2.508\, \text{Å}\) and that of Ge2–Ge2 atoms is \(R_2 = 2.505\, \text{Å}\). The basal plane of pGe is puckered,
and the buckling distance (determined by the vertical height difference between the Ge1 and Ge2 layers shown in Figure 1a) is \( h = 1.308 \) Å, which is much larger than the corresponding values of pentagraphene\(^{3,18}\) and pentasilicene.\(^{29}\) This is attributed to the largest atomic radii of germanium atoms. Moreover, the bond angle of Ge2−Ge1−Ge2 is \( \theta_1 = 105.78^\circ \), and the bond angle of Ge1−Ge2−Ge1 is \( \theta_2 = 106.07^\circ \), indicating distinct sp\(^3\) hybridized bonds. To assess the dynamic stability of the 2D pGe, we have measured the phonon spectrum of the pentagonal structure, as shown at the bottom of Figure 1a. The presence of imaginary vibration in the phonon dispersion shows that the pGe structure is dynamically unstable. The detailed analysis shows that the two soft modes around the \( \Gamma \)-point are associated with the tricoordinated Ge2 atoms because the Ge2 atoms are arranged in an unfavorable, highly buckled configuration and they prefer transforming into sp\(^3\) hybridization, causing soft modes to collapse the 2D sheet. Overall, the Ge2 atoms tend to distort the pentagonal structure, leading to the dynamical instability.

To improve the structural stability of pGe, the key is to stabilize the buckled structure of Ge2 atoms. Thus, a powerful route to enhance the stability is chemical functionalization, which has been widely used to tune the properties of low-dimensional nanostructures,\(^{39,44}\) including the Ge-based nanostructures.\(^{39,44}\) Indeed, previous experimental studies have shown that both hydrogenated- and methylated-germanene sheets with graphene-like lattices are stable at room temperature.\(^{33,36,42}\) The fluorinated-germanene sheet and various chemically functionalized group-IV 2D nanosheets hereafter demonstrated that these chemical functionalizations are energetically more favorable than those of the 2D hexagonal sheet. These results can be understood from the differences in the tricoordinated Ge2 atoms with nearly sp\(^3\) hybridization in the pGe sheet and the partially delocalized \( \pi \) orbital arising from sp\(^3\)-like hybridization. Therefore, the Ge2 atoms in the 2D pGe sheet are chemically more active than the Ge atoms in the hexagonal germanene.

To address the enhancement in the thermal stability induced by hydrogenated and fluorinated functionalization, we have further performed ab initio molecular dynamics (AIMD) simulation at 300 and 500 K, respectively. The 2D chemically functionalized sheet is expanded to a 3 × 3 supercell consisting of 90 atoms. Figure 2 presents the total energy fluctuations and the final structures of the functionalized H−pGe−H and F−pGe−F sheets at the end of AIMD simulations, and the corresponding results for the pristine pGe sheet are also shown for comparison. The time step is set to be 2 fs, and 2.5 and 5 ps AIMD simulations are carried out for the pristine pGe and functionalized pGe nanostructures, respectively. As clearly shown in Figure 2a, the average values of the total energies of the pGe sheet at 300 and 500 K are decreased. As a consequence, its final nanostructure has been broken almost completely after a period of 2.5 ps. In contrast, the functionalized pGe sheets are found to sustain their integrated nanostructures during the AIMD simulations at 300 and 500 K.

### Table 1. Structural Parameters and Energy Gaps of the Optimized Germanene-Based 2D Nanomaterials Chemically Functionalized by Hydrogenation and Fluorination\(^{a}\)

| Conformation | \( R_1 \) (Å) | \( R_2 \) (Å) | \( R_3 \) (Å) | \( \theta_1/\theta_2 \) (deg) | \( h \) (Å) | \( a \) (Å) | \( E_b \) (eV) | \( E_b \) (PBE) | \( E_b \) (HSE06) |
|--------------|--------------|--------------|--------------|-----------------|----------|----------|--------------|---------------|----------------|
| H−pGe−H      | 2.48         | 2.47         | 1.56         | 106.3/105.2     | 1.32     | 5.57     | 0.52         | 1.92           | 2.60           |
| F−pGe−F      | 2.51         | 2.53         | 1.78         | 105.4/106.9     | 1.29     | 5.69     | 3.47         | 1.39           | 2.09           |
| H−GeF\(^4\)  | 2.47         | 2.47         | 1.56         | 106.3/105.2     | 0.73     | 4.09     | 0.25         | 0.95           | 1.62           |
| F−Ge−F\(^4\) | 2.54         | 2.54         | 1.79         | 1.08            | 0.58     | 4.29     | 3.21         | 0.00           | 0.17           |

\(^{a}\) \( R_1 \) (Ge1−Ge2 bond length in Å), \( R_2 \) (Ge2−Ge2 bond length in Å), \( R_3 \) (Ge−H/Ge−F bond length in Å), \( \theta_1/\theta_2 \) (Ge1−Ge2/Ge1−Ge2−Ge1 angle in deg), \( h \) (buckling distance in Å), \( a \) (lattice constant in Å), \( E_b \) (binding energy in eV/per atom), \( E_b \) (PBE) (in eV), and \( E_b \) (HSE06) (in eV)
The observed total energy fluctuations of both hydrogenated and fluorinated pGes are almost zero, as evidenced by the zoomed insets in Figure 2b,c. Furthermore, it is noted that the total energy fluctuations of the hydrogenated and fluorinated...
pentagraphenes at room temperature are much larger than those of the corresponding functionalized pGe cases, indicating that the functionalized pGe could be energetically more favorable. Taking the calculated results shown above into account, hydrogenation and fluorination of 2D pGe sheets lead to not only dynamical stability but also thermal stability at room temperature and even at a temperature of 500 K. Next, we will focus on the electronic structures of the hydrogenated and fluorinated pGes, and the electronic properties of the pristine pGe will not be considered because of its dynamically unstable nanostructure.

The calculated electronic structures and the corresponding partial density of states (PDOSs) of the hydrogenated and fluorinated pGes are shown in Figure 3. Clearly, H-pGe-H is a semiconductor with an indirect band gap of 1.92 eV at Perdew–Burke–Ernzerhof (PBE) level. Its valence bond maximum (VBM) is located at the M-point, and its conducting bond minimum (CBM) is located at about 1/2 along the Γ–M path in the momentum space. This feature is different from that of the hydrogenated pentasilicene and hydrogenated pentagraphene, whose CBMs are located at the Γ-point. The underestimation of electronic band gap in the framework of PBE functional is well-known; thus, we have carried out Heyd–Scuseria–Ernzerhof (HSE)06 functional calculations to obtain more accurate results. The electronic structures obtained by PBE and HSE06 are analogous, whereas HSE06 gives significant modification on band gap to 2.60 eV, showing that hydrogenation can tune the electronic structure of pGe from metal to semiconductor. Furthermore, we found that both PBE and HSE06 band gaps are approximately 1 eV larger than the corresponding value for germanane. On the basis of the analysis of charge density distribution, as shown in Figure 3a, the VBM of H-pGe-H is mainly contributed by the Ge2–Ge1 bonding state and partially by the Ge2–Ge2 bonding state, indicating the σ characters. In contrast, its CBM is composed of the Ge2–H antibonding state, indicating the σ* characters.

For the fluorinated pGe, it is also an indirect band gap semiconductor. The band structure calculation at PBE level reports a band gap of 1.39 eV, and the HSE06-calculated result is essentially identical to the PBE one, except for the increased
Figure 4. Effects of tensile strain on the total energies and electronic structures of the hydrogenated and fluorinated pGes. The electronic band structures of (a) the hydrogenated pGe and (d) the fluorinated pGe under different tensile strains. The band structures shown here are calculated by the PBE functional. Biaxial strain dependence of the band gap ($E_g$) of (b) the hydrogenated pGe and (e) the fluorinated pGe. The total energy and buckling distance ($h$) variations as a function of biaxial strain for (c) the hydrogenated pGe and (f) the fluorinated pGe, confirming that the unstrained nanostructure corresponds to the lowest total energy. Band structures based on the PBE functional under certain external tensile strains are listed in the figures.
The electronic structures of H–pGe–H and F–pGe–F shown in Figure 3 are very similar. However, hydrogenated and fluorinated decorations in pGe give rise to distinct influences on the characters of VBM and CBM states. For instance, the charge density of F–pGe–F reveals that both Ge and F atoms have significant contributions to the VBM state, which is verified by the PDOS result, and its CBM state is originated from strong covalent bonds formed between Ge2 and F atoms. The differences between the PDOSs of hydrogenated and fluorinated decorations are attributed to the considerably different electronegativities of the adatoms. The electronegativity is increased from H to Ge and F atoms. The Ge2 atoms are regarded as acceptors in the hydrogenated case of H–pGe–H nanostructure, whereas these become donors in the fluorinated case of F–pGe–F nanostructure. More importantly, the characters of VBM and CBM states, arising from different chemical functionalizations, can be modified by external tensile strains.

The external strain has been widely used to tune the electronic structure and thermal properties of materials, and previous studies have shown that a topologically nontrivial phase can be achieved in the Ge-based 2D nanomaterials by tensile strain. Thus, we investigate the effects of biaxial strain on the electronic structures of hydrogenated and fluorinated pGes and hope that the indirect–direct band gap transition can be obtained for these functionalized pGes by tensile strain. In this study, the biaxial strain is stimulated by varying the in-plane lattice to a series of values, which are larger/smaller than those of the equilibrium structure. The strain imposed on the structure is defined as \( \varepsilon = (a - a_0)/a_0 \) where \( a_0 \) and \( a \) denote the lattice constants of the unstained and strained systems, respectively. Considering that the differences in the electronic structures obtained by PBE and HSE06 are concentrated on band gap values, we calculate the electronic structures at PBE level, as shown in Figure 4. Correspondingly, the HSE06 band gap values can be roughly estimated by scissor operation.

As explicitly shown in Figure 4a, a direct band gap at the M-point can be obtained for the H–pGe–H 2D sheet when \( \varepsilon = 6\% \) biaxial strain is applied. The presence of the indirect–direct semiconductor transition is favorable for its potential applications, and this phenomenon can be understood from the charge transfer between Ge2 and Ge1 atoms. In detail, once a tensile stretch is applied on the nanostructure, the Ge1–Ge2 bond length is increased from 2.479 Å to 2.533 Å when \( \varepsilon = 6\% \) and the buckling distance \( (h) \) is also monotonously decreased. As a result, Ge1 has superior electronegativity compared to that of the Ge2 atoms and charge transfers from Ge2 to Ge1 atoms, which is confirmed by its CBM charge density and PDOS results shown in Figure S1. As the tensile stretch increased monotonously, the Ge1 atom's induced energy level with the \( \sigma_{pp}^* \) character is shifted downward at the M-point and the Ge2 atom's induced energy level (at 1/2 of M–\( \Gamma \) path) with the \( \sigma_{pp}^* \) character is shifted upward. Once the critical strain of \( \varepsilon = 6\% \) is achieved, the \( \sigma_{pp}^* \)-characterized state eventually becomes CBM to replace the original \( \sigma_{pp}^{10} \) state, leading to the indirect–direct transition for the hydrogenated pGe. Generally, the band gap of H–pGe–H is decreased in a linear way with a continuous increase in stretch strain. When a compressing tensile is applied, conversely, the \( \sigma_{pp}^{10} \)-characterized level is shifted upward and the \( \sigma_{pp}^* \)-characterized one is shifted downward. As a consequence, the indirect band gap is reduced as a compressing strain is exerted on the H–pGe–H nanosheet, as shown in Figure 4b. For the 2D H–pGe–H nanosheet, it is interesting to find that not only its band gap can be tuned in a wide range of 1.25–1.92 eV (1.95–2.62 eV at HSE06 level according to scissor operation), but also the indirect to direct band gap transition can be obtained for this semiconductor. Most importantly, the strain range calculated in our study is generally achievable for experimental realization. For instance, the 2D MoS2 nanomaterial can be subjected to an external strain of 11%. Specifically, we noticed that the lattice constant of the zinc blende MgSe film is 5.89 Å, which can be served as a substrate for applying the epitaxial strain by molecular beam epitaxy. Owing to the interaction between the film and the substrate via the weak van der Waals interactions, the biaxially strained H–pGe–H with \( \varepsilon = 6\% \) can be realized similar to the 2D sheet grown on the BN substrate. Therefore, the hydrogenated pGe is expected to have practical applications in the field of nanoelectronics.

However, in the case of fluorinated pGe, we found that the indirect band gap character is maintained at the tensile range of \( \varepsilon = -8 \) to 10%. The absence of the indirect–direct band gap transition, in sharp contrast to that in H–pGe–H, is attributed to the high electronegativity of the fluorine atoms. The electronic structure evolutions of F–pGe–F under stretch strain can be described in the following steps: (1) At equilibrium position, its indirect band gap is determined by the \( \sigma_{pp}^* \)-characterized VBM at the M-point and the \( \sigma_{pp}^{10} \)-characterized CBM at about 2/5 of the M–\( \Gamma \) path. (2) As a small stretch strain (\( \varepsilon = 2\% \)) is applied, the \( \sigma_{pp}^{10} \)-characterized CBM is shifted upward. We stress that the \( \sigma_{pp}^{10} \)-characterized CBM is robust to the biaxial strain because the F atoms always serve as acceptors and the Ge2 atoms here are donors. The external tensile strain, including both stretch and compressing, can effectively tune the Ge1–Ge2 coupling, whereas the \( \sigma_{pp}^{10} \)-featured CBM is less influenced and only relative shift is observed, as shown in Figure S2b. Meanwhile, the Ge1 atom's induced energy level at the X-point is lifted toward the Fermi level, which is due to the increasing charge density around the Ge1 atoms. (3) When the stretch strain is further increased, the \( \sigma_{pp}^{10} \) state governed by the Ge1 atoms becomes the VBM as \( \varepsilon = 4\% \) is satisfied, leading to the change in VBM location. This phenomenon can also be understood from the significant increase in the calculated PDOSs of the Ge1 atoms, as demonstrated in Figure S2. Thus, the indirect band gap is determined by the VBM at the X-point and the CBM located at the M–\( \Gamma \) path. (4) As the stretch strain is further increased (\( \varepsilon > 4\% \)), the VBM at the X-point is found to be more pronouncedly influenced, in contrast to the robust CBM. Therefore, the band gap is reduced with increasing biaxial strain. Additionally, the zinc blende CdSe with lattice constant \( a = 6.05 \) Å can be a potential substrate for the experimental realization of \( \varepsilon = 6\% \) strain. On the other hand, when the nanosheet is subjected to a compressing strain, its CBM is influenced and moves toward the Fermi level. The band gap of F–pGe–F is found to monotonously decreased, as shown in Figure 4e. Overall, the electronic structure of F–pGe–F is shown to be effectively modulated by the external strain.

Furthermore, we have considered that the tetracoordinated Ge atoms are likely to be substituted by other group-IV elemental atoms. The aim is to understand the influences of incorporation of C/Si/Sn/Pb substitutional atoms on the pGe structure and its electronic structures. For simplicity, we focus only on the hydrogenated pGe with substitutional doping, and the two Ge1 atoms are replaced by the C, Si, Sn, and Pb atoms, respectively. Hence, the four doped configurations, as
still preserved (space group no. 113). From the viewpoint of it is found that the symmetry of the doped nanostructures is 2, and the corresponding electronic structures are then calculated. These four doped H

\[ \text{H}_2 \] (buckling distance in Å), \[ \text{R} \] as \[ \sigma \] features of various dopings. In addition, \[ \Gamma \] bond length in Å), \[ \theta \] and \[ \text{Ge}_2 \] bond length in Å), \[ \text{X} \] angle in deg), \( h \) (buckling distance in Å), \( a \) (lattice constant in Å), \( E_b \) (binding energy in eV/per atom), \( E_{g-PBE} \) (in eV), and \( E_{g-HSE06} \) (in eV).

schematically shown in Figure 5, are represented as H–pGe–C–H, H–pGe–Si–H, H–pGe–Sn–H, and H–pGe–Pb–H. These four doped H–pGe–H nanostructures are optimized, at first, with their structural parameters summarized in the Table 2, and the corresponding electronic structures are then calculated to assess the effects of various dopings. In addition, it is found that the symmetry of the doped nanostructures is still preserved (space group no. 113). From the viewpoint of energy in terms of \( E_b \), the four substitutional dopings are all energetically favorable. Moreover, the lattice constant \( \langle a \rangle \), the Ge2–X bond length \( (R_b) \), and the buckling distance \( h \) increased as the atomic number increased from C to Pb. Correspondingly, the \( \sigma \)-featured CBM substantially reduced as \( R_b \) increased from C to Pb, and eventually, it almost vanished for Pb doping. The band gaps of the doped system can be varied in a wide range (1.16–4.35 eV by hybrid functional calculation), as shown in Figure 5, and Si, Sn, and Pb dopings give rise to high electron mobility at the M-point. In addition, it is worth mentioning that the electronic bands along the M–Γ path are doubly degenerate as a result of symmetry protection by the space group. This double degeneracy can be broken by semidoping, that is, only one Ge1 atom is replaced by the C atom, and the expected results have been confirmed by our calculation shown in Figure S3b. Thus, the substitutional dopings can be utilized to modulate the electronic structures of the H–pGe–H 2D sheet.

**CONCLUSIONS**

In summary, we use first-principles calculations to study the structural stability and electronic properties of the pGe modulated by chemical functionalization. Although the pristine 2D pGe is energetically unfavorable, the functionalized pGes decorated by hydrogenation and fluorination are found to be dynamically and thermally stable. We have shown that the hydrogenated and fluorinated pGes are stable even at a high temperature of 500 K. Both hydrogenated and fluorinated-Ge pentagonal germanes are semiconductors with indirect band gaps of 1.92 and 1.39 eV (2.60 and 2.09 eV by the HSE06 functional), respectively. The electronic structures of the functionalized pGes can be effectively modulated by biaxial tensile strain. More importantly, our calculations reveal that the indirect to direct band gap transition can be achieved for the hydrogenated pGe sheet by 6% biaxial strain. Furthermore, we show that the band gap of H–pGe–H can be further tailored from 1.16 to 4.35 eV by heteroatom doping (C/Si/Sn/Pb). Therefore, the chemically functionalized pGes are expected to possess robust structural stability and excellent electronic properties, allowing Ge-based 2D nanosheets to have many potential applications in the future.

**COMPUTATIONAL METHODS AND MODELS**

The first-principles calculations within density functional theory are utilized in the Vienna ab initio simulation package (VASP). Projector-augmented wave pseudopotentials in the form of the PBE functional are used for electronic exchange-correlation potential. The electronic wave functions of valence electrons are expanded using plane-wave basis sets with a cutoff energy of 500 eV. For structural optimizations, the exchange-correlation potential is described by the generalized gradient approximation. The PBE functional is used in most of our calculations, and the hybrid HSE06 functional is also employed for more accurate electronic structure calcula-
The convergence criteria for total energy and force component are set to be $10^{-6}$ eV and 0.001 eV/Å. A vacuum layer of 30 Å is set in the plane normal direction to minimize image interactions. The Monkhorst—Pack set of $25 \times 25 \times 1$ k-points for the 2D structures is used to sample the BZ for the geometry optimization, and a denser grid of $31 \times 31 \times 1$ is used for electronic structure computations. The phonon dispersions are calculated by density functional perturbation theory (DFPT) as implemented in the CASTEP code. All AIMD simulations are performed in the canonical (NVT) ensemble via the VASP code. The temperature is controlled by the Nosè—Hoover algorithm at 300 and 500 K. The equations of motion are integrated using the velocity Verlet algorithm.

### ASSOCIATED CONTENT

**Supporting Information**

Influences of tensile strain on the electronic structures of hydrogenated pGe (Figure S1); influences of tensile strain on the electronic structures of fluorinated pGe (Figure S2); calculated electronic band structures based on the PBE functional of full C doping and semi C doping (Figure S3) (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: zenghui@yangtzeu.edu.cn. Tel: +86-25-85866608. Fax: +86-25-85866600.*

**ORCID**

Hui Zeng: 0000-0002-7657-6714

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We are grateful to Prof. B.-G. Wang and Prof. H.-J. Zhang for electronic structure simulations as well as inspirational discussions. Most computational simulations are performed in the High Performance Computing Center of Nanjing University. This work is financially supported by Natural Science Foundation of China (Grant Nos. 11303022, 11347010, and 11404037), and China Postdoctoral Science Foundation (Grant No. 2015MS571729). H.Z. would like to thank the “Chutian Scholar” Program that is sponsored by Hubei Government.

### REFERENCES

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, 306, 666.
2. Cahangirov, S.; Top sclak, M.; Aktürk, E.; Sahin, H.; Ciraci, S. Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium. *Phys. Rev. Lett.* 2009, 102, No. 236804.
3. Xu, Y.; Yan, B.; Zhang, H.-J.; Wang, J.; Xu, G.; Tang, P.; Duan, W.; Zhang, S.-C. Large-gap Quantum Spin Hall Insulators in Tin Film. *Phys. Rev. Lett.* 2013, 111, No. 136800.
4. Voon, L. C. L. Y.; Sandberg, E.; Agra, R. S.; Farajian, A. A. Hydrogen Compounds of Group-IV Nanosheets. *Appl. Phys. Lett.* 2010, 97, No. 163114.
5. Hossma, M.; Scalise, E.; Sankaran, K.; Pourtois, G.; Afnansev, V. V.; Ste meas, A. Electronic Properties of Hydrogenated Silicene and Germanene. *Appl. Phys. Lett.* 2011, 98, No. 223107.
6. García, J. C.; de Lima, D. B.; Assali, L. V. C.; Justo, J. F. Group IV Graphene- and Graphane-Like Nanosheets. *J. Phys. Chem. C* 2011, 115, 13242–13246.
7. Vogt, P.; Padova, P. D.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M. C.; Resta, A.; Eate, B.; Lay, G. L. Silicene: Compelling Experimental Evidence for Graphene-like Two-Dimensional Silicene. *Phys. Rev. Lett.* 2012, 108, No. 155501.
8. Chen, L.; Liu, C.-C.; Feng, B.; He, X.; Cheng, P.; Ding, Z.; Meng, S.; Yao, Y.; Wu, K. Evidence for Dirac Fermions in a Honeycomb Lattice Based on Silicon. *Phys. Rev. Lett.* 2012, 109, No. 056804.
9. Davila, M. E.; Xian, L.; Canghong, S.; Rubio, A.; Lay, G. L. Germanene: A Novel Two-Dimensional Germanium Allotrope Akin to Graphene and Silicene. *New J. Phys.* 2014, 16, No. 095002.
10. Li, L.; Lu, S.-Z.; Pan, J.; Qin, Z.; Wang, Y.-Q.; Wang, Y.; Cao, G.-Y.; Du, S.; Gao, H.-J. Buckled Germanene Formation on Pt(111). *Adv. Mater.* 2014, 26, 4820–4824.
11. Amamou, W.; Odenthal, P. M.; Bushong, E. J.; ŌHara, D. J.; Luo, Y. K.; van Baren, J.; Pinchuk, I.; Wu, Y.; Ahmed, A. S.; Katoch, J.; Bockrath, M. W.; Tom, H. W. K.; Goldberger, J. E.; Kawamura, R. K. Large Area Epitaxial Germanene for Electronic Devices. *2D Mater.* 2015, 2, No. 035012.
12. Zhu, F.-F.; Chen, W.-J.; Xu, Y.; Gao, C.-L.; Guan, D.-D.; Liu, C.-H.; Qian, D.; Zhang, S.-C.; Jia, J.-F. Epitaxial Growth of Two-Dimensional Stanene. *Nat. Mater.* 2015, 14, 1020–1025.
13. Zeng, H.; Zhi, C.; Zhang, Z.; Wei, X.; Wang, X.; Guo, W.; Bando, Y.; Golberg, D. White Graphenes: Boron Nitride Nanoribbons via Boron Nitride Nanotube Unwrapping. *Nano Lett.* 2010, 10, 5049–5055.
14. Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* 2012, 7, 699–712.
15. Mak, K. F.; Shan, J. Photonics and Optoelectronics of 2D Semiconductor Transition Metal Dichalcogenides. *Nat. Photonics* 2016, 10, 216–226.
16. Li, L.; Yu, Y.; Ye, G. J.; Ge, Q.; Ou, X.; Wu, H.; Feng, D.; Chen, X. H.; Zhang, Y. Black Phosphorous Field-Effect Transistors. *Nat. Nanotechnol.* 2014, 9, 372–377.
17. Carvalho, A.; Wang, M.; Zhu, X.; Rodin, A. S.; Su, H.; Neto, A. H. C. Phosphorene: from Theory to Applications. *Nat. Rev. Mater.* 2016, 1, 16061.
18. Zhang, S.; Zhou, J.; Wang, Q.; Chen, X.; Kawazoe, Y.; Jena, P. Penta-graphene: A New Carbon Allotrope. *P. Natl. Acad. Sci. U.S.A.* 2015, 112, 2372–2377.
19. Wang, F. Q.; Yu, J.; Wang, Q.; Kawazoe, Y.; Jena, P. Lattice Thermal Conductivity of Penta-graphene. *Carbon* 2016, 105, 424–429.
20. Wang, Z.; Dong, F.; Shen, B.; Zhang, R. J.; Zheng, Y. X.; Chen, L. Y.; Wang, S. Y.; Wang, C. Z.; Ho, K. M.; Fan, Y.-J.; Jin, B.-Y.; Su, W.-S. Electronic and Optical Properties of Novel Carbon Allotropes. *Carbon* 2016, 101, 77–86.
21. Eknollahzadeh, H.; Dariani, R. S.; Fazeli, S. M. Computing the Band Structure and Energy Gap of Penta-graphene by using DFT and GW0 Approximations. *Solid State Commun.* 2016, 229, 1–4.
22. Lopez-Bezanilla, A.; Littlewood, P. B. σ-π-Band Inversion in a Novel Two-Dimensional Material. *J. Phys. Chem. C* 2015, 119, 19469–19474.
23. Li, F.; Tu, K.; Zhang, H.; Chen, Z. Flexible Structural and Electronic Properties of a Pentagonal B2C Monolayer via External Strain: A Computational Investigation. *Phys. Chem. Chem. Phys.* 2015, 17, 24151–24156.
24. Zhang, S.; Zhou, J.; Wang, Q.; Jena, P. Beyond Graphitic Carbon Nitride: Nitrogen-Rich Penta-CN2 Sheet. *J. Phys. Chem. C* 2016, 120, 3993–3998.
25. Zhou, J.; Wu, M. M.; Zhou, X.; Sun, Q. Tuning Electronic and Magnetic Properties of Graphene by Surface Modification. *Appl. Phys. Lett.* 2009, 95, No. 103108.

DOI: 10.1021/acsomega.6b00439

ACS Omega 2017, 2, 171–180

ACS Omega
(26) Zhou, J.; Wang, Q.; Sun, Q.; Jena, P. Electronic and Magnetic Properties of a BN Sheet Decorated with Hydrogen and Fluorine. **Phys. Rev. B** **2010**, *81*, No. 085442.

(27) Zheng, F.-B.; Zhang, C.-W. The Electronic and Magnetic Properties of Functionalized Silicene: A First-Principles Study. **Nanoscale Res. Lett.** **2012**, *7*, 422.

(28) Zhang, C.-W.; Yan, S.-S. First-Principles Study of Ferromagnetism in Two-Dimensional Silicene with Hydrogenation. **J. Phys. Chem. C** **2012**, *116*, 4163–4166.

(29) Ding, Y.; Wang, Y. Hydrogen-induced Stabilization and Tunable Electronic Structures of Penta-Silicene: A Computational Study. **J. Mater. Chem. C** **2015**, *3*, 11341–11348.

(30) Li, X.; Zhang, S.; Wang, F. Q.; Guo, Y.; Liu, J.; Wang, Q. Tuning the Electronic and Mechanical Properties of Penta-graphene via Hydrogenation and Fluorination. **Phys. Chem. Chem. Phys.** **2016**, *18*, 14191–14197.

(31) Wu, X.; Varshney, V.; Lee, J.; Zhang, T.; Wohlwend, J. L.; Roy, A. K.; Luo, T. Hydrogenation of Penta-graphene Leads to Unexpected Large Improvement in Thermal Conductivity. **Nano Lett.** **2016**, *16*, 3925–3935.

(32) Bianco, E.; Butler, S.; Jiang, S.; Restrepo, O. D.; Windl, W.; Goldberger, J. E. Stability and Exfoliation of Germanane: A Germanium Graphane Analogue. **ACS Nano** **2013**, *7*, 4414–4421.

(33) Jiang, S.; Butler, S.; Bianco, E.; Restrepo, O. D.; Windl, W.; Goldberger, J. E. Improving the Stability and Optical Properties of Germanane via One-step Covalent Methyl-termination. **Nat. Commun.** **2014**, *5*, 3389.

(34) Restrepo, O. D.; Krymowski, K. E.; Goldberger, J.; Windl, W. A First Principles Method to Simulate Electron Mobilities in 2D Materials. **New J. Phys.** **2014**, *16*, No. 105009.

(35) Wang, X.-Q.; Li, H.-D.; Wang, J.-T. Induced Ferromagnetism in One-Side Semihydrogenated Silicene and Germanene. **Phys. Chem. Chem. Phys.** **2012**, *14*, 3031–3036.

(36) Jiang, S.; Biancoa, E.; Goldberger, J. E. The Structure and Amorphization of Germanane. **J. Mater. Chem. C** **2014**, *2*, 3185–3188.

(37) Jiang, S.; Arguilla, M. Q.; Cultrara, N. D.; Goldberger, J. E. Covalently-Controlled Properties by Design in Group IV Graphane Analougues. **Acc. Chem. Res.** **2015**, *48*, 144–151.

(38) Zhao, J.; Zeng, H. Chemically Functionalized Germanene for Spintronic Devices: A First-Principles Study. **Phys. Chem. Chem. Phys.** **2016**, *18*, 8908–9815.

(39) Tang, Q.; Zhou, Z. Graphene-Analogue Low-Dimensional Materials. **Prog. Mater. Sci.** **2013**, *58*, 1244–1315.

(40) Butler, S. Z.; et al. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene. **ACS Nano** **2013**, *7*, 2898–2926.

(41) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. **Nat. Chem.** **2013**, *5*, 263–275.

(42) Li, T.; Goldberger, J. E. Atomic-Scale Derivatives of Solid-State Materials. **Chem. Mater.** **2015**, *27*, 3549–3559.

(43) Hu, L.; Zhao, J.; Yang, J. First Principles Study of Fluorine Substitution on Two-Dimensional Germanane. **J. Phys.: Condens. Matter** **2014**, *26*, No. 335302.

(44) Kuila, T.; Bose, S.; Mishra, A. K.; Khanra, P.; Kim, N. H.; Lee, J. H. Chemical Functionalization of Graphene and its Applications. **Prog. Mater. Sci.** **2012**, *57*, 1061–1105.

(45) Pinchuk, I. V.; Odenthal, P. M.; Ahmed, A. S.; Amamou, W.; Goldberger, J. E.; Kawakami, R. K. Epitaxial co-deposition Growth of CaGe2 Films by Molecular Beam Epitaxy for Large Area Germanane. **J. Mater. Res.** **2014**, *29*, 410–416.

(46) Si, C.; Liu, J.; Xu, Y.; Wu, J.; Gu, B.-L.; Duan, W. Functionalized Germanane as a Prototype of Large-Gap Two-Dimensional Topological Insulators. **Phys. Rev. B** **2014**, *89*, No. 115429.

(47) Zhang, R.-W.; Ji, W.-X.; Zhang, C.-W.; Li, S.-S.; Li, P.; Wang, P.-J. New Family of Room Temperature Quantum Spin Hall Insulators in Two-Dimensional Germanene Films. **J. Mater. Chem. C** **2016**, *4*, 2088–2094.