Communication

Structural, phononic and electronic properties of Ge-doped γ-graphynes: A first-principles study

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ABSTRACT

Three stable Ge-doped γ-graphyne-like structures have been systematically studied by first principles calculations based on density functional theory (DFT). These analogues were derived by substituting carbon atoms alternately with Ge atoms in the hexatomic ring of γ-graphyne family and referred to as GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3. These novel systems were found to have planar structures with Ge atoms staying at hexagons with sp²-hybridization. Their dynamical stabilities were confirmed from calculated phonon dispersion spectrums, and their electronic band structures show direct band gap semiconducting behaviors with the band gaps of 1.186 eV, 0.967 eV and 0.828 eV, respectively, indicating that Ge-doping can effectively increase the band gap of pristine γ-graphyne family materials.

1. Introduction

Since the successful synthesis of graphene in 2004 [1], its extraordinary properties such as electrical conductivity [2], tensile strength [3], transmittance [4] and thermal conductivity [5] have been extensively studied, and the results show its intriguing performance and the application potential as two-dimensional carbon materials. The rise of graphene has also stimulated the research interest in other two-dimensional carbon materials and, subsequently, graphynes have become the focus of attention as new planar allotropes of carbon. The γ-graphyne, the most simplest structure among graphynes, was first proposed in 1987 by Baughman et al. [6]. It consists of sp and sp² hybridized carbon atoms, and has innovative two-dimensional network structure with hexagonal rings linked by one acetylenic linkage. It was also predicted to be thermostable and semiconducting with a band gap of 1.2 eV by the extended Hückel theory (EHT) [6]. Furthermore, other members of possible γ-graphyne structures, such as γ-graphdiyne [7] (i.e., hexagonal rings linked by two acetylenic linkages), γ-graphyne-3 [8] (i.e., hexagonal rings linked by three acetylenic linkages) were also proposed theoretically in 1990’s. The successful synthesis of large-scale γ-graphdiyne (simply referred to as graphdiyne) on the surface of Cu [9] also stimulated the further research on graphynes. Cui et al. [10] found the strain-induced semiconductor-semimetal transition in γ-graphdiyne, and Dirac cone-like electronic structures were obtained by increasing the uniaxial tensile strain. Kang [11] and Long et al. [12] calculated the electronic properties of γ-graphyne and γ-graphdiyne, and found the band gaps of about 0.46 eV by using the GGA-PBE method. Such narrow band gaps may limit the application of the γ-graphyne family structures, and efforts on enlarging the band gap have been done. Singh et al. [13] uncovered that doping with B and N atoms can tune the band gaps of γ-graphyne family. Yan [14] investigated the Si-doped γ-graphdiyne and the result shows that this acetylenic structures constructed by silicon-carbon is stable, and the band gap is obviously widened. Bhattacharya et al. [15] studied the effect of fluorination of γ-graphyne and found that the fluorination can modulate the band gap and the wide band gap provides more flexibility for its use in nanoelectronic devices. Moreover, Qu et al. [16] proved that the elastic constants and the band gap of the γ-graphyne family can be also tuned by strain.

On the other hand, the structural, optical and electrical properties of GeC films, as a new type of semiconductor material with promising application, have been widely studied. These researches reveal that GeC films have a wide range of tunable optical band gap by radio frequency (RF) reactive magnetron sputtering, which is crucial for photovoltaic applications [17–19]. Furthermore, GeC single layer materials have also attracted the interest of many researchers [20,21].

Quite recently Zhang [22] et al. studied the electronic structure and thermodynamic properties of α-GeC-graphyne, and the calculation indicates that the most stable structure can be derived by substituting carbon atoms with Ge in six corners of α-graphyne. Besides, α-GeC-graphyne possesses excellent thermal stability and has a larger direct band gap of 1.078 eV. Motivated by this, in this work we aim to study
the possible existence of Ge-doped γ-graphynes and figure out whether the band gap can be modulated by Ge doping, using first principles calculations. The calculation method performed in this work is described in the Section 2. In Section 3, the geometric structures of Ge-doped γ-graphynes are optimized, and the phonon dispersion spectrum and electronic structures of the optimized Ge-graphyne monolayers are calculated and discussed. From these results, we have found that there are three stable planar GeC-graphyne monolayers which are obtained by substituting C atoms alternately with Ge at the six-membered ring of γ-graphyne family structures. They are referred as GeC-graphyne, GeC-graphdiyne, and GeC-graphyne-3, respectively, and have shown wider band gaps as compared to the corresponding pristine γ-graphyne family like structures. In Section 4, a brief conclusion is given.

2. Computational methods

All the calculations of structural and electronic properties are based on the density functional theory (DFT) with the projector-augmented-wave (PAW) method [23] in the Vienna ab initio Simulation Package (VASP) [24–26]. The exchange correlation potential is evaluated by Perdew-Burke-Ernzerh of (PBE) [27] functional using the generalized gradient approximation (GGA) [28]. The cutoff energy of plane wave is 550 eV. A 11×11×1 Monkhorst-pack [29] k-point mesh was used to sample the Brillouin zone. Vacuum layer of 15 Å was applied perpendicular to the sheets to avoid the interlayer interactions. In all these calculations the convergence criteria for total energy in the self-consistent field iteration was set to be $10^{-6}$ eV and the optimizations have been carried out by keeping the volume of the unit cell constant until the Hellmann–Feynman force component on each atom is less than $10^{-3}$ eV/Å.

The vibrational properties are calculated using PHONOPY [30] code, which can directly use the force constants calculated by density functional perturbation theory (DFPT) [31] as implemented in the VASP code. Here, 2×2×1 supercells are considered for all structures [32].

3. Results and discussion

3.1. Structural optimization and characterization

In order to find the possible existence of planar structures with Ge doping in γ-graphyne family, we have performed a comprehensive survey on structure optimization. The initial planar and buckled structures were constructed by substituting C atoms with Ge atoms in hexatomic ring alternately and outright, as well as on acetylenic link chain alternately and symmetrically. It was found that GeC monolayers, obtained by alternately substituting C atoms with Ge atoms at the six-membered rings, are stable structures. These GeC-graphyne-like monolayers are referred to as GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3. They are presented in Fig. 1, and the corresponding ratio of C and Ge atoms were 3:1(Fig. 1(a)), 5:1(Fig. 1(b)) and 7:1 (Fig. 1(c)), respectively.

The optimized structural parameters of pure γ-graphyne family and GeC-graphynes monolayers were given in Table 1. Compared with the pristine γ-graphyne family, the lattice constant of GeC-graphynes are larger, and the average energy are higher. It mainly because the C - Ge bond length in doped structure is longer than C - C bond in the undoped structure, and also the chemical potential of the Ge atom is higher than that of the C atom.

In particular, we found that energetically, the γ-graphyne is the most stable structure (−8.583 eV/atom), followed by the γ-graphdiyne (−8.460 eV/atom), and the γ-graphyne-3 (−8.396 eV/atom) is relative high in energy among the three pristine sheets, indicating that the more the acetylenic linkages in chains between hexagons, the higher the relative energy is. This energy order is also kept when three C atoms at the corners of hexagons were substituted by three Ge atoms. Namely, for a given concentration $N_{Ge}/(N_{Ge}+N_{C})$, the number of Ge/C per

![Fig. 1. Schematic structures of the GeC-graphyne (a), the GeC-graphdiyne (b) and the GeC-graphyne-3 (c) sheets, respectively.](image)

<table>
<thead>
<tr>
<th>Item</th>
<th>γ-graphyne</th>
<th>γ-graphyne-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of acetylenic linkages in chain</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Lattice Constant(Å)</td>
<td>6.890</td>
<td>8.230</td>
</tr>
<tr>
<td>Total Energy(eV/cell)</td>
<td>−102.998</td>
<td>−84.016</td>
</tr>
<tr>
<td>Energy per atom(eV)</td>
<td>−8.583</td>
<td>−7.001</td>
</tr>
</tbody>
</table>

![Fig. 2. The total energy per atom as a function of concentration (NGe/(NGe+NC)) for pristine and doped graphyne family like structures.](image)
unit cell), from 0 to 0.25, as shown in Fig. 2, the graphyne-like GeC sheet is the most preferential compared with the graphdiyne- or the graphyne-3-like GeC sheets.

To better understand the hybridization properties in GeC-graphynes monolayers, we carried out a detailed structure analysis of GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3. The labeled bond lengths and bond angles are presented in Fig. 3(a)–(c) and Fig. 3(d)–(f), respectively. These results show that bond angles $\alpha_1$, $\alpha_2$, $\alpha_5$ and $\alpha_6$ are near 120° in GeC-graphyne, indicating that bond 1 is a single bond with sp$^2$ hybridization between C and Ge atoms. But $\alpha_3$ and $\alpha_4$ are 180°, manifesting that bond 3 is acetylene linkage formed by C atoms with sp hybridization. In addition, bond 2 and bond 4 are both single bonds. In GeC-graphdiyne, it is found that bond angles $\alpha_1$, $\alpha_2$, $\alpha_7$ and $\alpha_8$ are near 120°, this indicates that bond 1 is a single bond formed by C and Ge atoms with sp$^2$ hybridization. But bond angles $\alpha_{3,6}$ are 180°, therefore, bonds 3 and 5 are acetylene linkages and bond 4 is

Fig. 3. The Ge-C and C-C bonding nature of the GeC graphyne (a), the GeC-graphdiyne (b) and the GeC-graphyne-3 (c). The indexes 1–8 denote the locations of various bonds. The bonding angle nature of the GeC graphyne (d), the GeC-graphdiyne (e) and the GeC-graphyne-3 (f) are indicated by $\alpha_1$–$\alpha_{10}$, respectively.

Fig. 4. The bond lengths of the GeC graphyne (a), the GeC-graphdiyne (b), and the GeC-graphyne-3 (c). The bond angles of the GeC graphyne (d), the GeC-graphdiyne (e), and the GeC-graphyne-3 (f).
single bond, forming by C atoms with sp hybridization. Besides, bond 2 and 6 are also single bonds. In GeC-graphyne-3, bond angles $\alpha_1$, $\alpha_2$, $\alpha_9$ and $\alpha_{10}$ are near 120°. Hence, bond 1 is a single bond consisting of C and Ge atoms with sp$_2$ hybridization. Whereas, bond angles $\alpha_3$–$\alpha_8$ are 180°, this illustrates that bonds 3, 5 and 7 are acetylene linkages and bonds 4 and 6 are single bonds, forming by the C atoms with sp hybridization. Then, both bonds 2 and 8 are single bonds. In these stable plane structures, C and Ge atoms form small hexatomic rings due to sp$_2$ hybridization.

Fig. 5. Top panels: The phonon dispersions of the GeC-graphyne (a), the GeC-graphdiyne (b), and the GeC-graphyne-3 (c). Bottom panels: The phonon dispersions of the $\gamma$-graphyne (a), the $\gamma$-graphdiyne (b), and the $\gamma$-graphyne-3 (c).

Fig. 6. The electron localization functions of the GeC-graphyne (a), the GeC-graphdiyne (b), and the GeC-graphyne-3 (c) (upper top panels), the $\gamma$-graphyne (a), the $\gamma$-graphdiyne (b), the $\gamma$-graphyne-3 (c) (bottom panels).

An important finding of our work is that the systems cannot converge to periodic lattices when germanium atoms are asymmetrically distributed on the $\gamma$-graphyne family, because the different radiuses of C and Ge induced the different bond lengths of Ge-C and C-C bonds. Besides, it is hard to form a stable two-dimensional planar structure when hexatomic rings are all substituted by Ge atoms, and the system converges to a high buckled honeycomb structure with a tiny band gap of 0.523 eV, indicating that sp$_3$ hybridization takes precedence over sp$_2$ hybridization between Ge atoms. Now, our optimized monolayers keep the similar symmetry with pristine structure because of sp$_2$ hybridization which came from Ge atoms alternately distributed on the hexatomic ring.
3.2. Phonon dispersion

The phonon dispersion spectrum was calculated to study the structural stability of three new GeC-graphynes (Fig. 5). It is found that the frequency of GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3 are all positive, indicating that these new planar structures are stable. All GeC-graphynes and pristine graphynes have three acoustic branches at \( \Gamma \) point, but the former structures exhibit more flat phonon dispersions than the later especially between 20 and 30 THz. Thus the phonon transport and electron phonon coupling characters of GeC-graphynes structures might be different from those of \( \gamma \)-graphyne family crystals. Moreover, there are some distinct differences in phonon spectrums among GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3. In low frequency mode (0–30 THz), the phonon dispersion of the GeC-graphyne is more obvious, while phonon dispersions are more flat with narrow bandwidths in other two structures. In the range of 30 to 40 THz, the GeC-graphdiyne has no phonon frequency which distinct from GeC-graphyne and GeC-graphyne-3. In the range of 40–50 THz, however, GeC-graphyne has no phonon frequency, which has significant difference with GeC-graphdiyne and GeC-graphyne-3. Between 60 and 70 THz three structures all present high frequency modes because of sp bonds, which are same with pristine graphyne family structures but graphene [33].

3.3. Charge distribution

The electron localization function (ELF) and Bader charges [34] were calculated to check the chemical bonding of the C and Ge atoms in GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3 systems, and the results are given in Fig. 6 and Table 2. The C atom at the hexatomic rings are labeled as C*, and other sites at the chain are also labeled as shown in Fig. 6 and the color denotes the renormalized ELF values. The values of 1.00 and 0.50 correspond to fully localized and fully delocalized electrons, respectively, while the value of 0.00 refers to very low charge density. From Fig. 6 we can see that all of these three structures exhibit strong covalent bonding characters between C and Ge.
Ge atoms, as the electrons are highly localized between them (e.g., the red colors between C2/C* and Ge in upper panels of Fig. 6(a)-(c)). Bader charge analysis shows that the electric charges transfer from the Ge atoms to the C atoms (−1.33e~−1.36e). And half of the transferred electrons transfer to the C atoms at the hexatomic ring while the other half transfer to the C atoms at the chain. The results also reveal that the electrons are equally distributed on the hexatomic rings of γ-graphyne family. But in GeC-graphynes, there is the charge transfer at the hexatomic rings. This causes the difference of conjugate π-bonds between the pristine and the doped graphynes. The substitution of Ge atoms changes the distribution of electrons.

3.4. Electronic structures

Electronic structure calculations show that GeC-graphyne, GeC-graphdiyne and GeC-graphyne-3 are all semiconductors. From the band structure diagrams with three different GeC-graphynes (see Fig. 7), we know that the band structures changed a lot with Ge doping.

As shown in the Fig. 7(a), the highest valence band of the GeC-graphyne was located at Μ point, while the lowest conduction band was located in the vicinity of Μ point. Therefore, this structure is approximatively direct band gap semiconductor with the largest band gap of 1.186 eV. The shapes of valence band and conduction band are symmetric displaying parabolic nature. Band widths are narrower than those of pristine γ-graphyne, indicating that electrons are localized.

The band structure of GeC-graphdiyne is different from that of GeC-graphyne. As shown in Fig. 7(b), it has a direct band gap of 0.965 eV with the top of the valence band and the bottom of the conduction band all located strictly at Γ point. Compared with GeC-graphyne, GeC-graphdiyne has a narrower band width. This indicates that the electrons are more localized in GeC-graphdiyne. However, the bands of γ-graphdiyne system are steep with a wider bandwidth as shown in the bottom figure in Fig. 7(b). This means that the electrons in γ-graphdiyne are strongly delocalized.

GeC-graphyne-3 is also a direct band gap semiconductor with a minor gap (0.828 eV). The gap is opened at Μ point (see Fig. 7(c)). Like GeC-graphyne, it has a parabolic band shape near the Fermi level. It also has a wider band gap and more bands compared with γ-graphyne-3. Besides, the bands are more flat, this means a stronger localization of the electrons. All these structures exhibit direct band gaps, and the results reveal that the substitution of Ge atoms changes the electronic structures of γ-graphyne family. These indicate their potential applications, particularly for optoelectronic applications [32].

To show clearly the capability of Ge atom for band gap opening, we provided the band gaps of undoped and doped structures in Table 3, where the results of undoped graphene are in good agreement with the
previous calculation [8,11,13,35]. By comparing, we found that the Ge doping can tune the band gap of γ-graphyne family structures effectively. In addition, with the increase of composition of C and Ge atoms, the band gaps of GeC-graphynes are enlarged monotonously. Hence, the band gap in such systems can be tuned through introducing Ge atom and changing the number of the acetylene linkage.

Although three GeC-graphynes have similar monolayer flat sheet with graphene-like structures and semiconductor characteristics, they have different electronic structures. To further understand the contribution of C and Ge elements on electronic properties, we calculated the total densities of states (Total DOS) (Fig. 8(ii)–(iii)), local densities of states (LDOS) (Fig. 8(iii)) and partial densities of states (PDOS) (Fig. 8(iv)) of GeC-graphyne, GeC-graphidyne and GeC-graphyne-3, respectively. Figs. 8a–c (ii) show that all three GeC-graphynes exhibit obvious band gaps due to Ge-doping. Compared with γ-graphyne (Fig. 8a(i)), γ-graphidyne (Fig. 8b(i)) and γ-graphyne-3 (Fig. 8c(i)), the total densities of states of three GeC-graphynes show more sharp peaks. It can be seen from the LDOS (Figs. 8a–c (iii)) that even though the contribution from Ge atom (yellow curves) is very small compared with the contribution from C atoms (pink curve), the behaviors of the Total DOS (second row panels) show significant changes in the shape and width even when substituting a few C atoms with Ge atoms. The PDOS (seen in Figs. 8a–c (iv)) clearly shows that only the z components of the p-orbital contribute to the states at the top of the valence bands and the bottom of the conduction bands in all GeC-graphyne structures. For GeC-graphyne, below the Fermi level, p\(_z\)-orbital and p\(_\sigma\)-orbital show same component between ~1.2 eV to ~2.25 eV. But all s-orbital and three components of p-orbital contribute to states density of conduction bands in the range of 2.5 eV to 3.6 eV. Besides, GeC-graphidyne and GeC-graphyne-3 show similar distributions with GeC-graphyne.

4. Conclusions

We have found three promising stable monolayer plane structures, GeC-graphyne, GeC-graphidyne and GeC-graphyne-3. The geometric structure, stability, and electronic structures of these new structures have been systematically studied. The calculated electronic structures show that these GeC-graphyne sheets are semiconductors. Among them, GeC-graphyne is an approximatively direct band gap (from M to C) semiconductor with the largest band gap of 1.186 eV. Nevertheless, GeC-graphidyne is a strict direct band gap semiconductor with the band gap of 0.965 eV, the top of valence band and the bottom of conduction band are located at the Γ point of Brillouin zone, while GeC-graphyne-3 has the direct band gap at M point with the energy gap of 0.828 eV. Compared with the pure graphene family, Ge substitution in these systems can tune the band gap efficiently. The interesting results of ELF show that the charge transfer in C-Ge systems leads to the change of conjugated \(\pi\)-bond, which may affect the thermal stability of these materials. Another important finding is that the system cannot converge to a periodic lattice when germanium atoms are distributed asymmetrically in the γ-graphyne, because the asymmetric strain due to asymmetric distribution of Ge atoms. However, when C atoms were symmetrically substituted by germanium on the acetylenic chain, the system converges to a high buckled honeycomb structure with a tiny band gap. Finally, adjusting the Ge-doped proportion can modulate the band gap of γ-graphyne family structures effectively. In conclusion, these new carbon analogues cannot only enrich the database of carbon allotropes, but also have potential application for electronic device, optoelectronics and molecular sieves.

References