Structural and electronic properties of $\text{Si}_m\text{C}_n$ graphyne-like monolayers

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The structural stability and the electronic properties of the $\text{Si}_m\text{C}_n$ graphyne-like monolayers with $18,18,24$-graphyne type of structure have been systematically studied using a transferable and reliable semi-empirical Hamiltonian (referred as SCED-ICAO method). Three stable $\text{Si}_m\text{C}_n$ graphyne-like structures are obtained including the flat $\text{SiC}$ and $\text{Si}_2\text{C}_8$ graphyne-like sheets and the slightly buckled $\text{Si}_2\text{C}_8$ graphyne-like sheet with a small buckling of 0.05 Å. The co-existence of the $sp$ and $sp^2$ types of the hybridization between silicon and carbon atoms is found in these systems. The electronic properties of these systems are found to be highly dependent on the stoichiometry of C and Si elements. The flat $\text{SiC}$ and $\text{Si}_2\text{C}_8$ graphyne-like monolayers have semi-conductor properties with the energy gap of 0.955 eV and 0.689 eV, respectively. The slightly buckled $\text{Si}_2\text{C}_8$ graphyne-like monolayer, on the other hand, behaves like a tiny gap material.

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1. Introduction

In recent years, in addition to the extensive interest on the graphene, other 2D carbon allotropes have also attracted more attention. Among them, the graphene is the most interesting one [1–4]. Not only because it has abundant carbon bonds, big conjugate structure, wide spacing, but it also has excellent chemical stability and semiconductor performance, and therefore, it is considered to be the most stable compound among artificial, unnatural carbon allotrope [5]. These interesting properties make the graphene promised material in the applications for electronics, energy storing, and optoelectronics [6–9]. Furthermore, theoretical studies based on the DFT (density functional theory) have shown that the graphene has a better conductivity than the graphene [10]. The studies on the electronic structure of the multilayer graphene ribbon also show that the graphene nanoribbons are semiconductors with suitable band gaps similar to the bulk silicon and the gaps decrease as the widths of nanoribbons increase [11]. In addition, other members of graphene family have also been obtained by inserting some $-$C=C$-$ links between two hexagonal rings, such as alpha, beta, gamma graphyne [12].

Graphdiyne, a member of the graphene family, has been realized experimentally by Li et al. [6]. They have successfully synthesized the large area of graphdiyne films (with 3.61 cm$^2$) on the surface of copper via a cross-coupling reaction using hexaethylbenzene [6]. The SEM and TEM results show that this film can grow continuously on large surface area of copper and has a good flexibility. This work also shows that the graphdiyne has a plane structure with a few defects. The conductivity of this film is $2.516 \times 10^{-4}$ S/m. On the other hand, Jiao et al. [13] have calculated the capacity of the adsorption of $\text{H}_2$ and $\text{CH}_4$ molecules on the graphdiyne surface, and found that the adsorption energy has a maximum value when the gas molecule is in the center of the cell of the graphdiyne. Zheng et al. [14] studied the physical properties and electronic structure of the multilayer graphdiyne using the first principles method. They obtained the stable multilayer graphdiyne structure and found the dependence of gap on the intensity of electric field.

The successful synthesis of the graphdiyne has also stimulated the study of the 2D derivatives of the graphdiyne. A series of interesting properties of the 2D derivatives of the graphdiyne such as the superconductivity, electricity and mechanics have been predicted [15,16]. Enyashin and Ivanovskii [15] studied the stability and electronic structure of the graphdiyne doped with Fluorine, and found that its electronic properties are highly dependent on stoichiometry of C and F elements. Ongun et al. [16] predicted a new 2D BN sheet which is similar to the structure of the $\alpha$-graphyne. They studied the heating and hydrogenation processes, and found that $\alpha$-BNyne nanostructures can form stable and durable 2D extended structures with interesting chemical and physical properties.
On the other hand, SiC-based materials, one of the interesting semiconducting materials, are widely used in aviation, aerospace, automobile, machinery, electron engineering and chemical engineering industry owing to its excellent performance of thermal conductivity, abrasion, and corrosion resistance. It is also found that SiC nanostructures have more outstanding properties [17–20], which attracted tremendous attentions. For instance, Sun [21] made a deep study on synthesizing SiC nanowires (structure with sp^3 type of the hybridization) and SiC nanotubes (structure with sp^2 type of the hybridization), and Yu et al. [22] studied the stability of 2D SiC honeycomb and tubular structures based on DFT (density functional theory). They found that the sp^2 hybridization could exist between Si and C atoms in the SiC graphitic-like structures. These previous studies indicate that the sp^2 and sp^3 hybridization can form between Si atom and C atoms.

It is of great curiosity to know what will happen when the Si atoms are introduced into graphene system. Will such single layer sheet be stable? Could the sp hybridization form between Si and C atoms? Will such systems possess energy gap and show the semiconductor nature? To answer these questions, we have systematically studied Si_{1n}C_{m} single layered systems [23] by substituting C atoms with Si atoms in the framework of the graphene structure. We adopted a highly efficient quantum mechanics molecular dynamics (MD) scheme based on the self-consistent and environment-dependent (SCED) Hamiltonian in the framework of linear combination of atomic orbitals (LCAO) [24, 25] (referred as SCED–LCAO–MD). We have obtained three stable Si_{1n}C_{m} graphyne-like monolayers, namely, the flat SiC graphene, the flat Si_{1}C_{8} graphene, and the slightly buckled Si_{1}C_{9} graphene, respectively. We found the co-existence of the sp and sp^3 types of the hybridization between silicon and carbon atoms in these Si_{1n}C_{m} graphene-like monolayers. We also found that the electronic properties highly depend on the stoichiometry of C and Si elements: the flat SiC and Si_{1}C_{8} graphene-like monolayers have semi-conductor properties, while, the slightly buckled Si_{1}C_{9} graphene-like monolayer is a tiny gap material. Furthermore, the electronic densities of states (DOS) at the Fermi level are found mainly contributed from the p_{z}-band (perpendicular to the graphyne-like sheet), indicating that the pi-bonds play an important role in stabilizing the Si_{1n}C_{m} graphene-like monolayers. In the following section, we will first briefly describe our molecular dynamics simulation scheme. In Section 3, we will discuss the structural stability, the electronic band structure, and the chemical bonding nature of these three systems in terms of the composition and the orbital hybridization. The structure properties at high temperatures are also discussed in this section. The conclusions will be finally given in Section 4.

2. Molecular dynamics simulation scheme

To realize the goal illustrated above, more than 120 initial structures need to be performed in the MD simulations including finite temperatures simulations. It will be a daunting task to survey these many initial structures with ab initio simulations based on the density functional theory (DFT). Therefore, we adopted an highly efficient molecular dynamics scheme based on the SCED–LCAO Hamiltonian (see Eq. (1)) developed by Louisville group [24, 25].

\[
H_{\text{ab initio}} = \frac{1}{2} \left( \epsilon_{i}^{s} + \epsilon_{j}^{s} \right) K(R_{i}) S_{ab}(R_{i}) \left( \epsilon_{i}^{s} + \epsilon_{j}^{s} \right) + \frac{1}{2} \left[ (N_{i} - Z_{i}) U_{i} + (N_{j} - Z_{j}) U_{j} \right] S_{ab}(R_{i}) \left( N_{i} - Z_{i} \right) \left( N_{j} - Z_{j} \right)
+ \frac{1}{2} \left[ \sum_{k_{i}} \left( N_{k_{i}} V_{k_{i}}(R_{i}) - Z_{i} V_{k_{i}}(R_{i}) \right) + \sum_{k_{j}} \left( N_{k_{j}} V_{k_{j}}(R_{j}) - Z_{j} V_{k_{j}}(R_{j}) \right) \right] S_{ab}(R_{i}) \left( N_{k_{i}} V_{k_{i}}(R_{j}) - Z_{i} V_{k_{i}}(R_{j}) \right)
\]

(1)

In Eq. (1), the first term describes the two-center interaction (via the on-site energies \( \epsilon_{i}^{s}(\epsilon_{j}^{s}) \), the scaling function \( K(R_{i}) \), and the overlap function \( S_{ab}(R_{i}) \)). The second term describes the charge distribution on sites i (N_{i}) and j (N_{j}) (where Z_{i} and Z_{j} are valence electrons and Hubbard-like term on site i (j), respectively). The third term contains the three-center (directly) and multi-center (indirectly via the charge distribution on site k (N_{k})) interactions between electron and electron (via the potential energy function \( V_{k} \)) and the electron–ion (via the potential energy function \( V_{k} \), respectively). The most advantageous feature of the SCED–LCAO Hamiltonian, compared to other existing semi-empirical Hamiltonians, is that it has a framework to allow the self-consistent determination of charge-redistribution and the inclusion of the environment-dependent multi-center interactions on the same footing. These are two key ingredients for an appropriate description of bond-breaking and bond-forming processes that play dominant roles in the structure reconstruction of complex systems. The total energy (see Eq. (2)) in the framework of the SCED–LCAO Hamiltonian includes the band structure energy (the first term), the correction term from the double-counting of electrons (the second and third terms), and ion–ion repulsive energy (the fourth term), where the band structure energy is obtained by solving the self-consistent generalized eigenvalue equation. The force acting on each atom (see Eq. (3)) can be carried out according to the Hellmann–Feynman theory [26, 27].

\[
E_{\text{total}} = \sum_{i} n_{i} \epsilon_{i} + \frac{1}{2} \sum_{i} \left( Z_{i}^{2} - N_{i}^{2} \right) U_{i} - \frac{1}{2} \sum_{i} \sum_{j \neq i} N_{i} N_{j} V_{ij}(R_{ij})
+ \frac{1}{2} \sum_{i} \sum_{j \neq i} Z_{i}^{2} Z_{j} U_{ij} - \frac{1}{2} \sum_{i} \sum_{j \neq i} Z_{i} Z_{j}^{2} U_{ij} - \frac{1}{4} \sum_{i} N_{i} N_{j} N_{k} N_{l} V_{ijkl}(R_{ijkl}) + \frac{1}{2} \sum_{i} \sum_{j \neq i} \sum_{k} Z_{i} Z_{j} Z_{k} U_{ijk}
\]

(2)

\[
F_{i} = \sum_{j \neq i} \sum_{j} \left( c_{i}^{*} c_{j} \right) * c_{j} \left[ \frac{\partial H_{ij}}{\partial \epsilon_{i}} - \epsilon_{i} \frac{\partial S_{ab}}{\partial \epsilon_{i}} \right]
+ \frac{1}{2} \sum_{i} \sum_{j \neq i} \sum_{k} \left( Z_{i} Z_{j} - Z_{i} Z_{j} \right) \frac{\partial (E_{ij} / R_{ij})}{\partial \epsilon_{i}} \right), \quad l = x, y, z
\]

(3)

The SCED–LCAO Hamiltonian has shown to have the transferability, the reliability, the robustness, and the predictive power [24, 25, 28–30]. Molecular dynamics scheme based on the SCED–LCAO Hamiltonian (i.e., the SCED–LCAO–MD) has also shown its highly efficient capability, compared to the DFT-based first principle methods, and can be employed to optimize structures of large complex systems that are beyond the scope of the ab initio calculations. A comparison of the computational efficiency between the SCED–LCAO–MD method and the DFT method has been discussed in Ref. [25]. For detail description about the SCED–LCAO Hamiltonian, please refer Refs. [24, 25].

In this work we first checked the graphyne using the SCED–LCAO–MD method. The optimized C=C and C–C bond lengths are 1.278 Å and 1.436 Å, respectively. The results are in consistent with the DFT results with the full potential linear combination of atomic orbitals method [31] (i.e., 1.220 Å and 1.396 Å for C=C and C–C bond lengths, respectively). We then employed the SCED–LCAO–MD method to study the Si_{1n}C_{m} graphene-like monolayer structures. The time step in this molecular dynamics simulation is set to be 1.5 fs. The energy was converged to within 10^-5 eV, and the force criteria for a fully relaxation process was set to be less than 10^-4 eV/Å. To validate our simulation results, similar calculations using the DFT based VASP software [32–34] are also performed. We used the projector-augmented wave method (PAW) [35, 36] to describe the interaction between ions and electrons and the local-density approximations (LDA) to treat the electronic exchange–correlation energy. The criteria are set to be 10^-5 eV for the energy convergence with the plane-wave cutoff energy of 540 eV and 10^-4 eV/Å for the force in the relaxation process (i.e.,
the conjugate gradient algorithm). The Monkhorst–Pack scheme is used to sample the Brillouin zone, and a mesh of \(7 \times 7 \times 1\) \(k\)-point sampling is used for our simulation. The distance between two layers in the supercell is set to be 15 Å to avoid the interlayer interactions.

### 3. Results and discussions

#### 3.1. Structural stability

We have performed a systematic simulation on \(\text{Si}_{m}\text{C}_n\) graphyne-like monolayers with 18,18,24-graphyne type of structure [23]. Starting from the 18,18,24-graphyne structure, we substituted the carbon atoms by the silicon atoms at some special sites to form the initial configurations of the \(\text{Si}_{m}\text{C}_n\) graphyne-like structure. Various compositions including the SiC graphyne, the SiC\(_8\) graphyne, the SiC\(_9\) graphyne, and the SiC\(_{17}\) graphyne were considered. The schematic structures of the SiC, SiC\(_8\), and SiC\(_9\) graphyne-like sheets are shown in Fig. 1(a), (b) and (c), respectively.

The gray balls represent the carbon atoms and the yellow ones are Si atoms. In the structure optimization process, we first relaxed \(\text{Si}_{m}\text{C}_n\) graphyne-like systems with different super cells including \(2 \times 2\), \(3 \times 3\), and \(4 \times 4\) super cells. We found that the optimized structures are independent of the size of the super cells. We then systematically studied the structural and electronic properties of the \(\text{Si}_{m}\text{C}_n\) graphyne-like systems choosing the samples with the \(2 \times 2\) super cell. Furthermore, in order to understand whether the \(\text{Si}_{m}\text{C}_n\) graphyne-like systems prefer to the \(sp^2\) type of bonding (i.e. stabilize to a flat sheet) or a co-existence of the \(sp^2\) and \(sp^3\) hybridization (i.e., stabilize to a buckled sheet), we constructed two types of the initial configurations for each of these \(\text{Si}_{m}\text{C}_n\) graphyne systems, one is a flat sheet, and the other is a buckled sheet with the buckling between 0.01 and 0.5 Å. These initial structures are fully relaxed using the SED-LCAO–MD method mentioned above. Three stable \(\text{Si}_{m}\text{C}_n\) graphyne-like monolayers are obtained. They are the flat SiC graphyne, the flat SiC\(_8\) graphyne, and the slightly buckled SiC\(_9\) graphyne with the buckling of 0.05 Å.

Obtained cohesive energy \(E_{\text{cohesive}}\) per atom versus the lattice constant \(a\) for the relaxed SiC graphyne, the SiC\(_8\) graphyne, and the SiC\(_9\) graphyne are presented in Fig. 2(a), (b) and (c), respectively. The solid curves are the cohesive energies per atom for the structures relaxed from the initial flat sheets, and the dashed curves are cohesive energies per atom for the structures relaxed from the initial buckled sheets. The cohesive energy per atom is defined as \(E_{\text{cohesive}} = (E_{\text{total}} - N_S \times E_S - N_C \times E_C)/N\), where \(E_{\text{total}}\) (\(N\)) is the total energy (total number of atoms) of the \(\text{Si}_{m}\text{C}_n\) graphyne system, \(N_S\) the number of Si atoms, \(E_S\) the energy of isolated Si atom, \(N_C\) the number of C atoms, and \(E_C\) the energy of isolated C atom, respectively. We found that for the SiC graphyne and the SiC\(_8\) graphyne, both the initial flat and buckled sheets will finally stabilized to a flat sheet when the lattice constant \(a > 18.89\) Å (for SiC graphyne) and 16.16 Å (for SiC\(_8\) graphyne), respectively. While, in the case of smaller value of lattice constant \(a\), the relaxed structure with initial buckled sheets are lower in energy than that with the initial flat sheets. The optimized lattice constant \(a\) is 18.956 Å for the SiC graphyne, and 16.279 Å for the SiC\(_8\) graphyne, respectively. Both the initial flat and buckled sheets are finally stabilized to a flat sheet at the equilibrium and have the same cohesive energy per atom (–6.45 eV/atom) for the SiC graphyne and –7.82 eV/atom for the SiC\(_8\) graphyne, respectively. The above results indicate that the flat structure is the most stable structure for both SiC graphyne and SiC\(_8\) graphyne. The SiC\(_9\) graphyne, however, shows a special geometrical property. It can be seen from the inset of Fig. 2(c) that the cohesive energy per atom of the SiC\(_9\) graphyne with the initial buckled sheet is –7.59 eV/atom, slightly lower than the structure with the initial flat sheet at the minimum (\(a = 17.381\) Å). The buckling of stabilized SiC\(_9\) graphyne at the minimum is very small (0.05 Å), indicating that the SiC\(_9\) graphyne structure prefers to stabilize to a slightly buckled sheet. The obtained stable flat SiC and SiC\(_8\) sheets and the slightly buckled SiC\(_9\) sheet are also confirmed with DFT (LDA–PAW) calculations using VASP software [32–34]. The optimized lattice constants are 18.642 Å for the flat SiC, 15.610 Å for the flat SiC\(_8\) sheets, and 16.729 Å for the slightly buckled SiC\(_8\) sheet, respectively. The obtained buckling for SiC\(_8\) sheet is 0.01 Å.

To understand the hybridization properties in \(\text{Si}_{m}\text{C}_n\) graphyne-like monolayers, we carried out a detailed analysis on the obtained stable structures of SiC graphyne, SiC\(_8\) graphyne and SiC\(_9\) graphyne. The obtained bond lengths and bond angles are presented in Fig. 3 and Table 1, respectively. The indexes in Fig. 3(a)–(c) denote the position of each bonds, and the indexes in Fig. 3(d)–(f) denote the locations of each angles. It is found that in these three structures, (1) bonds 1, 4, and 6 are triple bonds and belong to the sp hybridization; (2) the bond 5 is a single bond, and is also of the type of the sp hybridization; while (3) bonds 2, 3, 7, and 8 possess the sp\(^3\) hybridization. For comparison, we also analyzed the stable structure of the pure carbon system, referred as 18,18,24-graphyne [23]. From this table, one can see that the bond angles \(\alpha_2\), \(\alpha_3\), \(\alpha_8\) and \(\alpha_9\) (shown in Fig. 3(d)) for SiC graphyne are 120.42\(^\circ\) and 119.79\(^\circ\). This nature is also found in the 18,18,24-graphyne (see the 5th column in Table 1) indicating that the hybridization of molecular orbitals at the corner of the hexagonal ring in the graphyne structure is slightly different from that of the graphene. This is due to the difference between three neighbor chains at the corner. This asymmetry also affects charge distribution in the system. The similar hybridization can also be found in SiC\(_8\) and SiC\(_9\) structures. The calculated bond length of the triple bonds 1, 4 and 6 for SiC graphyne are 1.598 Å, 1.587 Å and 1.582 Å, respectively, which are in good agreement with the previous calculation [37]. The bond length indicates that delocalized \(\pi\)-bonds exist in this system.

![Fig. 1. A schematic structure of the SiC graphyne (a), the SiC\(_8\) graphyne (b) and the SiC\(_9\) graphyne (c) sheets, respectively. The vectors \(\mathbf{a}_1\) and \(\mathbf{a}_2\) in each structure represent the lattice vectors of the primitive unit cell. The gray balls represent the carbon atoms and the yellow ones are Si atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
It is interesting that the bond angles $\alpha_1$, $\alpha_4$ to $\alpha_7$ are exactly 180° in the case of the SiC graphyne. The results reveal that the Si and C atoms can form not only the $sp^2$ type of bonding in the SiC graphitic-like structures and $sp^3$ type of bonding in the SiC bulk structures, but also the $sp$ type of bonding in the chain-like structures. That means SiC, like carbon, can have different types of bonding and form various allotropes. More interesting is that the $sp$ and $sp^2$ types of the hybridization between Si and C atoms could be co-existent in these structures. The $sp^2$ bonds are formed at the corners of the hexagons and the $sp$ bonds are formed in the chains. In the triple bonds with the $sp$ hybridization, one of the pi-bonds is parallel to the plane, perpendicular to the sigma bond; and the other is perpendicular to the plane. The pi-bond in the $sp$ hybridization is also perpendicular to the plane. These pi-bonds are delocalized and play the crucial role in stabilizing the SiC$_n$ graphyne-like monolayers. Furthermore, it is found that in the case of the slightly buckled Si$_2$C$_8$ graphyne these angles are not 180°, but are 176.1°, 177.66° and 178.7°, indicate again that the $sp$ hybridization in Si$_2$C$_8$ graphyne is slightly different from that in SiC graphyne and Si$_1$C$_9$ graphyne and the stable Si$_2$C$_8$ graphyne is a quasi-2D structure.

3.2. Electronic structure

To understand the effect of the stoichiometry of C and Si elements on the electronic properties of Si$_m$C$_n$ graphyne-like monolayers, we have analyzed the electronic properties of the SiC graphyne, the Si$_1$C$_9$ graphyne, and the Si$_2$C$_8$ graphyne from their band structures (Fig. 4), total densities of states (DOS) (upper panels in Fig. 5), and partial densities of states (PDOS) (bottom panels in Fig. 5) using the DFT-based VASP code [32–34]. From these results, we found that even though the three layered systems have the same graphyne-like structure; their electronic properties are quite different and strongly depend on the stoichiometry of C and Si elements. It can be seen from Fig. 4 that, differ from the 18,18,24-graphyne, the band gap is opened in the Si$_m$C$_n$...
graphyne-like monolayers, indicating that these systems become semiconductors through the substitution of C atoms with Si atoms. In particular, the SiC graphyne is an indirect band gap (e.g., from \( K \) to \( U \) points) semiconductor with the band gap of 0.955 eV. The bands are flat and the band widths are narrow, indicating that the electrons are more localized in the SiC graphyne system. The PDOS (seen in Fig. 5(a)) clearly show that the \( p \)-bands including the \( x \)-, \( y \)-, and \( z \)-components mainly dominate the bands at the top of the valence band, while, the \( s \)-bands dominate the band at the bottom of the conduction band.

On the other hand, the Si1C9 graphyne is a direct band gap (i.e., from \( M \) to \( M \) points as shown in Fig. 4(b)) semiconductor with the band gap of 0.689 eV. The valence and conduction band shapes near the Fermi level show parabolic nature and are symmetric. The band widths are wider than those of the SiC graphyne, indicating that the electrons in this system are less localized. Compared to the PDOS of the SiC graphyne, it is found that in the case of the Si1C9 graphyne (see Fig. 5(b)) only the \( z \) components of the \( p \)-bands dominate the states at the top of the valence bands and the bottom of the conduction bands. In another word, there are no \( s \)-states and \( p_x \) and \( p_y \) states near the Fermi level.

Quite different from the SiC graphyne and the Si1C9 graphyne, the Si2C8 graphyne has a tiny gap (0.06 eV) material with delocalized nature. In particular, a tiny gap-opening band is found as compared to the band structure of the graphene and graphyne. But such gap-opening point is found at \( M \) point near the Fermi level (see Fig. 4(c)), which is different from the graphene and the \( \alpha \)-graphyne (at the \( K \) point) [10]. Such properties can also be seen from the symmetric nature at the Fermi level of the PDOS (Fig. 5(c)). Furthermore, from the PDOS we can find that, similar to the case of the Si1C9 graphyne, the states near the Fermi level (i.e., the states at the top of the valence bands and the bottom of the conduction bands) are mainly from the \( z \)-components of the \( p \)-states. From the above results, we found that the electronic band structure of Si\(_m\)C\(_n\) based graphyne systems not only depends on the composition (i.e., \( m/(m+n) \)) but also strongly depend on the distribution of the Si atoms in the framework of the structures.

### 3.3. Temperature dependence of structure

To study the temperature dependence of structure, we also performed molecular dynamics simulations for these structures at certain temperatures. The time step in the molecular dynamics simulations was set to be 1.5 fs and the total steps for each annealing process was set 2000. Thus, each process was performed in 3 ps. There is no symmetry restriction in the simulation and a velocity scaling scheme (Berendsen thermostat) was used in thermodynamic simulations. The Si\(_m\)C\(_n\) graphyne systems were gradually heated from 0 K up to 3300 K. Fig. 6 shows the structures of the SiC graphyne, the Si1C9 graphyne, and the Si2C8 graphyne at different temperatures. We found that (1) the SiC graphyne sheet begins to distort when it is heated up to 700 K, while there are only a few bonds distorted in the Si1C9 (Si2C8) graphyne sheet even the system...
was heated up to 800 K (1000 K); (2) even though these three sheets have more distortion at certain high temperatures (e.g., 1400 K for SiC graphyne sheet, 1500 K for Si\textsubscript{1}C\textsubscript{9} graphyne sheet, and 2000 K for Si\textsubscript{2}C\textsubscript{8} graphyne sheet, respectively), they could return to their initial ground state structures after they are gradually cooled down to 0 K. These reversible heating/cooling processes are indicated by the two-way arrows between the first and the second columns or the second and the third columns in Fig. 6; (3) with further heating, these sheets begin to break when the temperature reaches 2350 K for the SiC graphyne sheet, 2600 K for the Si\textsubscript{1}C\textsubscript{9} graphyne sheet, and 3300 K for the Si\textsubscript{2}C\textsubscript{8} graphyne sheet (see the last column structures in Fig. 6), respectively. These broken sheets

Fig. 5. The total densities of states (DOS) (upper panels) and partial density of states (PDOS) (bottom panels) of the SiC graphyne (a), the Si\textsubscript{1}C\textsubscript{9} graphyne (b), and the Si\textsubscript{2}C\textsubscript{8} graphyne (c). In the PDOS, the black-solid curve is the s-band, the red-dotted, green-dashed, and blue-dash-dotted curves are p\textsubscript{x}, p\textsubscript{y}, and p\textsubscript{z}-bands, respectively. The Fermi level is at zero and represented by the gray dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. The structures of the SiC graphyne (a), the Si\textsubscript{1}C\textsubscript{9} graphyne (b), and the Si\textsubscript{2}C\textsubscript{8} graphyne (c) at various temperatures (indicated at the bottom of each structure). The two-way arrows indicate that the processes are reversible in the heating/cooling processes while, and the one-way arrows indicate the irreversible processes.
could not return to their original ground states. Namely, such heating processes are irreversible. This is indicated by the one-way arrows between the third and fourth columns in Fig. 6. Apparently, the SiC8 graphene sheet can keep its configuration at 1000 K in Fig. 6(c)). The C–C bonding nature at 2600 K in SiC8 graphene, 800 K for the Si1C9 graphene, 1000 K for the SiC8 graphene, respectively. They will be destroyed only when the temperature reaches 2350 K (for SiC graphene), or 2600 K (for SiC9 graphene), or 3300 K (for SiC8 graphene). When the temperature is below these values, the structures can return to the stable structure at 0 K after a gradually cooling process, indicating that SiC8 graphene-like monolayers could be considered as the potential candidate of 2D monolayer materials for the application to high temperature resistance at nanoscale.

4. Conclusions

We have obtained three stable Si(m)Cn graphene-like structures. The existence of these novel structures has been systematically studied through the structural relaxation, optimization, electronic structures, as well as the thermal stability. Our results show that the SiC graphene and Si(m)Cn graphene are stabilized to a flat sheet structure, while, the most stable SiC8 graphene is a slightly buckled structure with the buckling of 0.05 Å. The most interesting finding is that the sp hybridization not only exists between C atoms, but also exists between Si and C atoms, indicating the flexibility of Si–C bonding nature in the SiC systems. Another significant finding is that the electronic structures of the Si(m)Cn graphene are sensitive to the location of the Si atoms (i.e., the stoichiometry of C and Si elements). In SiC8 structure, all the six corner positions are occupied by the Si atoms, and a tiny gap appears at the M point. While in the SiC and the SiCn graphynes, only part of the corner positions are occupied by carbon atoms and an obvious band gap opens in these two systems. These two systems behave as a semiconductor with the energy gap of 0.955 eV for the SiC graphene and 0.689 eV for the SiC8 graphene, respectively. The study on temperature dependence reveals that the obtained structures are rather stable below 700 K for the SiC graphene, 800 K for the Si1C9 graphene, and 1000 K for the SiC8 graphene, respectively. The C–C bonding nature at 800 K, it still keeps its basic planar configuration. Even though the hexagonal rings are slightly deformed at 1500 K (see the structure of the SiC8 graphene at 1500 K in Fig. 6(b)), no buckling appears until the temperature up to 2200 K. With the temperature increases to 2600 K, fractures occur first at the corners of those hexagonal rings occupied by Si atoms, and then the cracking at the corners of those hexagons occupied by C atom occurs (e.g., the structure of the SiC8 graphene at 2600 K in Fig. 6(b)). In the case of the slightly buckled SiC8 graphene, we found that it keeps its symmetry until 1000 K (see the structure of the SiC8 at 1000 K in Fig. 6(c)). The C–C bond in the hexagonal rings has a little deformation at 2000 K (see the structure of the SiC8 graphene at 2000 K in Fig. 6(c)). Such deformations gradually lead to the change of the sp2 hybridization between Si and C atoms and the sp3 hybridization forms at high temperature. When the temperature reaches to 3300 K, the structure is distorted with the corrugation about 1.6 Å (e.g., the structure of the SiC8 graphene at 3300 K in Fig. 6(c)). From these analysis on the hybridization we also found that the bond breaking of the Si(m)Cn graphene systems always happens on the sp2 SiC bonds at the corner position of the hexagons with the increasing of the temperature. These breaks lead to the further distortion and break on the sp bonds and finally, the systems are totally distorted.

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