The structural stability and the strain-induced electronic properties of α-Si$_1$C$_7$-graphyne like monolayer

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Abstract

The structural stability, the strain-induced electronic properties of the α-Si$_1$C$_7$-graphyne monolayers have been systematically studied by first-principles calculations. The α-Si$_1$C$_7$-graphyne is stabilized to a flat sheet structure with lattice constant of 7.588 Å. Compared with α-graphyne, the Dirac-cone electronic structure disappeared due to the substitution of C atoms by Si atoms and a direct-band gap of 0.83 eV was found. The electronic properties of α-Si$_1$C$_7$-graphyne under the symmetrical biaxial and asymmetrical uniaxial strains is investigated. The calculated results reveal that the band gap decreased linearly under the biaxial strain, while the asymmetrical uniaxial strains along armchair direction could make the gap decrease in a parabolic trend. Quite different from the former cases, the effect of the strain along the zigzag direction on the band gap is decreased almost linearly in different range of the tensile strain. In particular, a transition from the direct to the indirect band gap was found at strain of 18%. These changes of the electronic property of α-Si$_1$C$_7$-graphyne under uniaxial strain are remarkably distinct. Compared with such cases, this result reveals that a strain-induced electronic structure transition occurs in α-Si$_1$C$_7$-graphyne.

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1. Introduction

In recent years, carbon-based nanostructures have attracted more attention for its interesting electronic and mechanical properties. Among them, the graphyne is the most interesting one [1–4]. Analogous to graphene, graphynes have same extraordinary properties such as high carrier mobility, stable chemical properties and strong mechanics properties. Owing to its abundant carbon bonds and big conjugate structure, researchers predicted that Graphyne-based material have potential applications in electronics, energy and optoelectronics [5–13]. In the carbon-based materials, acetylenic linkages (–C≡C–) can be inserted into some appropriate chemical bonds to expand the system [14]. So other new graphyne-based materials have been designed by inserting some acetylenic links between hexagonal rings. Moreover, theoretical studies based on the first-principle calculations predicted four members of graphyne family (alpha, beta, gamma and 6–6–12 graphyne), which shows a better conductivity compared with the graphene [15,16].

Recently, several theoretical groups reported strain-induced electronic properties. Yue et al. [17] found that different types of strain can modify and modulate the band gaps of graphyne and its family. The band gap was increasing by the biaxial tensile strain but it decreased when the compressive strain was applied. Cui et al. [18] discovered that the semiconductor-semimetal transition takes place by different type of strain in graphdiyne, i.e. Cranford and Buthler [19] found that the direction of the tensile strain and the carbon acetylenic linkages could strongly modulate the fracture strain of graphyne. Furthermore, Miao [20] group has fabricated the contrastive band gap engineering of strained graphyne nanoribbons (GNR) with armchair and zigzag edges. From these result, the electronic properties of graphyne-based materials could be modulated by applying external strain in a possible way.

SiC based materials, one of the interesting semiconducting materials, are widely used in electron engineering and chemical engineering industry owing to its excellent properties. In particular, opposite to the gapless graphene, two-dimensional SiC graphene-like sheet has been predicted to have wide fundamental bandgap [21], indicating the possibility of opening bandgap by substituting C atom with Si atoms in graphene. Stimulated by this, we are interested in whether the electronic band structures of graphyne could be changed by substituting Si atoms. Recently, we...
have studied the silicon-carbide graphyne-like monolayers, and indeed, we found a bandgap opening [22]. It is of great curiosity to know what will happen when some of C atoms in the gapless \( \alpha \)-graphyne system were substituted by the Si atoms, as we know that Si and C atoms can also have \( sp^2 \) hybridization [21]. Will such monolayer be stable? Will this structure can open an energy gap? and if yes, is it a direct or indirect band gap? Interestingly, can the energy band gap be tuned with strain? To answer these questions, we have systematically performed \( Si_6C_8 \) systems with \( \alpha \)-graphyne-like structures by substituting C atoms with Si atoms in the framework of the graphyne structure. To optimize this kind of structure, we have considered various configurations including (1) all the six corner positions are substituted by the Si atoms (i.e., \( Si_2C_6 \)), (2) the chain positions are substituted by the Si atoms (i.e., \( Si_4C_4 \)), and (3) three corner positions are substituted by the Si atoms (i.e., \( Si_1C_7 \)). By studying the stability through phonon disper-

Fig. 1. (a) A schematic structure of the \( \alpha \)-Si\(_1\)C\(_7\)-graphyne. The brown balls represent the carbon atoms and the blue ones are Si atoms. (b) The vibration and phonon dispersion of the \( \alpha \)-Si\(_1\)C\(_7\)-graphyne. (c) The distribution of charge density of \( \alpha \)-Si\(_1\)C\(_7\)-graphyne. (The red color represents the higher charge distribution and the lower one is represented by the blue color.) (d) The band structures of \( \alpha \)-graphyne and \( \alpha \)-Si\(_1\)C\(_7\)-graphyne, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. The schematic structure of \( \alpha \)-Si\(_1\)C\(_7\)-graphyne under various tensile strains. (a) Under biaxial tensile strains, where the rectangle indicates a supercell with length \( L_x \) and width \( L_y \); (b) under a uniaxial strain along the armchair direction; (c) under a uniaxial strain along the zigzag direction.
sion analysis, we found that the structure with the configuration (3) is stable. We then concentrated this structure in the present work and studied the strain effect on its electronic band structure. It was found that, in the absence of strain, the gap of $\alpha$-Si$_1$C$_7$-graphyne is opened and this structure shows a direct band gap semiconductor property. While, the band gap decreased linearly with increasing the biaxial external strain from 1% to 14%, and non-linearly by applying a uniaxial tensile strain along the armchair direction. But in the tensile strain along the zigzag direction, the band gap decreases linearly with different slopes in different ranges of the tensile strain. Moreover, the electronic densities of states (DOS) around the Fermi level are found mainly dominated from the $p_z$-orbital, which is perpendicular to the graphyne-like sheet. It indicates that the $\pi$ electrons play an important role in stabilizing the structures. In the following section, we will briefly describe our simulation scheme. In Section 3, the structural stability, the

![Graph showing the strain energy-strain relation for each case](image)

**Fig. 3.** (a) $L_y$ versus $L_x$ and (b) the band gap versus $L_x$ of $\alpha$-Si$_1$C$_7$-graphyne under biaxial tensile strains; (c) $L_x$ versus $L_y$ and (d) the band gap versus $L_y$ of $\alpha$-Si$_1$C$_7$-graphyne under a uniaxial strain along the armchair direction; (e) $L_x$ versus $L_y$ and (f) the band gap versus $L_y$ of $\alpha$-Si$_1$C$_7$-graphyne under a uniaxial strain along the zigzag direction. The strain energy–strain relation for each case is shown in the inset of (a), (c) and (e), respectively.
chemical bonding property and the electronic structure of this system under different types of strain were investigated. In Section 4, the conclusions will be finally given.

2. Simulation scheme

All calculations were performed by Density functional theory (DFT), implemented within the Vienna ab initio simulation package (VASP) [23–25]. We used the projector-augmented wave method (PAW) to describe the interaction between ions and electrons and the generalized gradient approximation (GGA) 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 650 eV and $10^{-4}$ eV/Å for the force in the relaxation process. The Monkhorst-Pack scheme is used to sample the Brillouin zone, and a mesh of $11 \times 11 \times 1$ 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. Moreover, the calculation of the phonon dispersion of $\alpha$-Si$_1$C$_7$-graphyne is performed by the PHONOPY code in this work, and a mesh of $3 \times 3 \times 1$ k-point sampling is used for such calculation.

3. Results and discussion

The $\alpha$-Si$_1$C$_7$-graphyne monolayer is constructed by substituting carbon atoms with silicon atoms at the alternative corners of the hexagons. The schematic structures of the $\alpha$-Si$_1$C$_7$-graphyne are given in Fig. 1(a). The brown balls represent the carbon atoms and the blue ones are Si atoms. In the structure optimization, the $\alpha$-Si$_1$C$_7$-graphyne monolayer is stabilized to a flat sheet with the lattice constant $a_0$ of 7.588 Å. The phonon dispersions for $\alpha$-Si$_1$C$_7$-graphyne sheet, are calculated and were shown in Fig. 1(b). It was found that frequencies of all modes are positive, indicating the stability of the $\alpha$-Si$_1$C$_7$-graphyne monolayer. The frequencies of acoustic modes are in the range of 0–10 THz, and the frequencies of optical modes are mainly in the range of 5–30 THz. While the phonon band of optical modes is dense and the width of the band is narrow. Due to the sp hybridization, there are some high frequency vibrational modes in the range of 60–70 THz, which is in good agreement with the previous calculations [26]. The distribution of the charge density of $\alpha$-Si$_1$C$_7$-graphyne under no strain is shown in Fig. 1(c). The charge density of the acetylenic linkages (C≡C bond) is obviously higher than those of C–C sp$^2$ bonds and C–Si sp$^2$ bonds, indicating that the C≡C bond is stronger than the other bonds. The electronic properties of the stable structure with no external strains were calculated, as shown in Fig. 1(d).

For $\alpha$-graphyne, the valence and the conduction band meet at K point at the Fermi level in the Brillouin-zone, and the Dirac-cone electronic structure can be obtained. On the other hand, for $\alpha$-Si$_1$C$_7$-graphyne, the Dirac-cone electronic structure is destroyed and the gap is opening with 0.83 eV at K point. Near the Fermi level, the valence band and conduction band are symmetric. Compared with $\alpha$-graphyne, the narrow band width indicates that the electrons become more localized in this system.

To understand whether the strain can induce a change in the electronic property of $\alpha$-Si$_1$C$_7$-graphyne, we considered this structure under three different types of strains: (I) symmetrical biaxial tensile strains (see Fig. 2(a)), where the rectangle (dash line) indicates the boundary of the supercell with length $L_a$ and width $L_b$; (II) a uniaxial tensile strain along the armchair direction (see Fig. 2(b)); and (III) a uniaxial tensile strain along the zigzag direction (see Fig. 2(c)). In our work, the strain is changed in 1% increments. For each different strain value, we make the corresponding structure fully relaxed to reach the lowest energy. Namely, under biaxial strain, $L_a$ and $L_b$ are stretched uniformly with the same ratio, and all atoms are fully relaxed. When an uniaxial strain is stretched, only one direction is stretched, while another direction is set to be free, which makes the whole system reach the lowest energy.

Fig. 3 shows the strain energy versus the strain, $L_y$ versus $L_x$, and the energy gap-strain relations of $\alpha$-Si$_1$C$_7$-graphyne under the three types of strains. In our calculations, the tensile strain is defined as $e = (a - a_0)/a_0$, where $a/a_0$ is the lattice constant with/without strain. The strain energy is defined as $E = E(e) - E(0)$; namely, the energy difference between systems with and without strain. In the case of symmetrical biaxial strains (see Fig. 3(a)), the $L_y$ vs. $L_x$ curve rises straightly. The strain energy monotonically increases with the increasing of the strain and suddenly decreases at 14% (see the insert of Fig. 3(a)). Such change is associated with some bonds broken in the structure. When the strain reaches to 15%, the structure is destroyed. The band gap, on the other hand, decreases from 0.83 eV to 0.29 eV with increasing the strain, as shown in Fig. 3(b). When the strain is applied along the armchair direction, $L_y$ vs. $L_x$ shows a parabolic curve, as revealed in Fig. 3(c), the structure was destroyed after the strain of 26%, as can be seen from the change of energy (the insert of Fig. 3(c)). Different from the case of the biaxial strain (Fig. 3(b)), the band gap under the uniaxial strain along the armchair direction decreases following a convex descending curve from 0.83 eV to 0.52 eV with increasing the strain value (Fig. 3(d)). When the strain is executed along zigzag direction, $L_y$ vs. $L_x$ curve shows a nonlinear curve (Fig. 3(e)). As shown in Fig. 3(f), the band gap is decreased almost linearly in the ranges of 0–16%, 16–23% and 23–26%. The changes of the slopes at 16% and 23% are found mainly due to the change of the top of the valence band from the k point around the middle of the G–S line to the G point and the flattening of the bottom of the conduction band (as can be seen from Fig. 10(d)).

To investigate the chemical bond properties in $\alpha$-Si$_1$C$_7$-graphyne monolayers under the strains, a detail analysis on the
relaxed structures was carried out. The obtained bonds under three types of strains are presented in Fig. 4(a)-(c) (the indexes denote the position of each bonds). The bond length vs strain relation curves are shown in Fig. 5(a)-(c). In the case of the biaxial strain, the bond 1 and 6 (i.e., the C–C sp² bond) increase from 1.41 Å to 1.52 Å, the bond 2 and 5 (i.e., the C–Si sp² bond) show an insensible change from 1.24 Å to 1.26 Å, while the bond 3 and 4 (i.e., the C–Si sp² bond) rise substantially from 1.77 Å to 2.15 Å, these bonds increase almost linearly with the increasing strain. Apparently, the C–Si sp² bonds show a quick increase under the strain. When the strain is exerted along the armchair direction, the bonds 1, 2, and 3 have a similar behavior to that under the biaxial strain, while bonds 4, 5 and 6 which are along the armchair direction increase quickly with respect to 3, 2 and 1, respectively, as shown in Fig. 5(b). When the structure is stretched along the zigzag direction, as seen in Fig. 5(c), the bond 1 (i.e., the C–Si sp² bond) and bond 3 (i.e., the C–C sp² bond) are elongated distinctly with increasing strain. Unlike the case of uniaxial strain along zigzag direction, the bond 4 (i.e., the C–C sp² bond along the armchair direction) and bond 6 (i.e., the C–Si sp² bond along the armchair direction) increase slightly in the range of 0–10% strain while they become shorter when the structure is stretched beyond this limit. Comparing these results under the three types of strains, we found that the C–C sp bonds (i.e., bonds 2 and 5 in Fig. 4(a)-(c)) change a little, while the bonds with sp² hybridization orientated to the direction of the strain change distinctly.

To investigate how the electronic property of Si1C7 graphyne-like monolayer is modulated by the strain, we analyzed the modulated electronic properties including the band structures (Fig. 6) and partial densities of states (PDOS) (Fig. 7) using the VASP code. Fig. 6(a)-(d) shows the electronic structure of Si1C7 graphyne under symmetrical biaxial tensile strain of 1%, 6%, 10% and 14%, respectively. We found that this structure is still a direct gap semiconductor, e.g., the bottom of conduction and the top of valence are still located at K point, but the gap becomes gradually smaller and smaller as the strain increases. Especially, when the strain reaches 14%, the bottom of the conduction band changes distinctly. Furthermore, we found that the energy bands become more flat with the increasing of the strain, revealing that π electrons become more localized under the symmetrical biaxial strains. The PDOS (see in Fig. 7) clearly shows that the pₓ-orbital and pᵧ-orbital are almost the same in the valence band, and are mainly located at −1.8 eV below the Fermi level. The pₓ-orbital, on the other hand, mainly dominates around the Fermi level. But when the strain reaches to 14%, the s-orbital, the pₓ and the pᵧ-orbital dominate the bottom of conduction band, and the pₓ-orbital below Fermi level still dominate the top of valence band.

On the other hand, Fig. 8(a)-(d) presents the band structure of α-Si1C7-graphyne under the armchair direction strain with a value of 1%, 10%, 19% and 27%, respectively. The band gap decreases from 0.83 eV to 0.52 eV with the increase of strain. In the process of increasing the strain, the symmetry of the band around the fermi level is broken. The strain drives the movement of band maximum point in the reciprocal space, the top of valence bands moves from the K point to the location between G and M point, but this sheet still shows a direct-band semiconductor. From the PDOS (as shown in Fig. 9(a)-(d)), we found that around the fermi level, the density of state is still dominated by the pₓ orbitals. Owing to the symmetry breaking in the Brillouin zone, the pₓ and pᵧ orbitals distribute differently with increasing strain, especially the pₓ orbitals show a larger contribution. As shown in Fig. 9(a)-(d), a detailed observation reveals that the pₓ and pᵧ bands below the Fermi level move up and the s-bands near the Fermi level move down under effect of strain, in agreement with the band structure shown in Fig. 8 (a)-(d).
Fig. 6. The band structures under a symmetrical biaxial tensile strain of (a) 1%, (b) 6%, (c) 10%, and (d) 14%, respectively.

Fig. 7. The partial density of state (PDOS) under a symmetrical biaxial tensile strain of (a) 1%, (b) 6%, (c) 10%, and (d) 14%, respectively.
Fig. 8. The band structures under a uniaxial tensile strain along the armchair direction of (a) 1%, (b) 10%, (c) 19%, and (d) 27%, respectively. The open circles denote the top/bottom of the valence/conduction bands.

Fig. 9. The partial density of state (PDOS) under a uniaxial tensile strain along the armchair direction of (a) 1%, (b) 10%, (c) 19%, and (d) 27%, respectively.
Fig. 10. The band structures under a uniaxial tensile strain along the zigzag direction of (a) 1%, (b) 9%, (c) 18%, and (d) 26%, respectively. The open circles denote the top/bottom of the valence/conduction bands.

Fig. 11. The partial density of state (PDOS) under a uniaxial tensile strain along the zigzag direction of (a) 1%, (b) 9%, (c) 18%, and (d) 26%, respectively.
top of valence band moves to the G point inducing an indirect-gap property. The change of the top of valence band reveals a transition from the direct to the indirect gap induced by the strain. Compared with other cases, such observation reveals that strain-induced direct gap-indirect gap semiconductor transition may take place in α-Si$_1$C$_7$-graphyne. While the strain is exerted greater than 25%, the top of valence band becomes wider and the bottom of conduction band becomes flat. The PDOS calculations (Fig. 11) reveal that the occupied states were dominated by $p_z$ orbital around the Fermi level. With increasing strain, the $s$ orbital, $p_x$ orbital and $p_y$ orbital gradually dominate the bottom of the conduction. Different from the case of armchair-strain, in the case of the zigzag-strain, the $p_x$-band and $p_y$-band below Fermi level almost did not move up, but these bands above the Fermi level moved down to 2.5 eV.

4. Conclusions

By means of the DFT (GGA-PAW) calculations, we have obtained the stable flat α-Si$_1$C$_7$-graphyne-like structure with the lattice constant of 7.588 Å. Comparing with α-graphyne, we found that when the C atoms were substituted by the Si atoms at the corners of hexagons, the Dirac-cone electronic structure was destroyed and a direct-gap of 0.83 eV appeared. The electronic properties of α-Si$_1$C$_7$-graphyne under symmetrical biaxial and asymmetrical uniaxial strains show remarkably interesting. These results reveal that the band gap can decrease linearly under biaxial strain while the asymmetrical uniaxial strains along armchair direction could make the energy gap decrease in a parabolic trend. The energy band gap of the sheet under the strain along the zigzag direction, on the other hand, is decreased almost linearly in different ranges of the tensile strain. From the results of the band structure and PDOS, it is found that, under the biaxial strains, the occupied states are dominated by $p_z$ orbitals around the Fermi level, and the conduction and valence bands near the Fermi level are symmetric. However, this symmetry is broken by the uniaxial strain. In particular, a strain induced direct-indirect gap transition takes place in α-Si$_1$C$_7$-graphyne under the uniaxial strain along the zigzag direction. Our results revealed that the electronic properties of graphyne-based materials could be modulated by applying external strain in a possible way, which may have potential applications.

References