SiₙC₁₃₋ₙ (n = 1 – 12) Clusters: An All-electron DFT Investigation

Xingyu ZHOU¹, Zhiqiang DING¹, Hao ZHANG¹, Jin GUO¹,², Hua NING¹,²*, Ying LIU³

¹ Guangxi Key Laboratory of Processing for Non-ferrous Metallic and Featured Materials, College of Physics Science and Technology, Guangxi University, Nanning 530004, P.R. China
² Guangxi Collaborative Innovation Center of Structure and Property for New Energy and Materials, School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin, 541004, P.R. China
³ Department of Physics, Hebei Normal University, Shijiazhuang 050016, Hebei, China

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The geometrical and electronic structures of SiₙC₁₃₋ₙ (n = 1 – 12) nanoclusters have been investigated using all-electron density functional theory (DFT) with the generalized gradient approximation (GGA). The binding energies, highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gaps, and the vibrational frequencies have been computed. We note that the binary clusters have a number of isomeric structures with lower symmetries and the stability of the clusters increases as the number of carbon atoms increases. As the number of silicon atoms increases, the lowest-energy structures of the SiₙC₁₃₋ₙ (n = 1 – 12) clusters transform from planar structures to three-dimensional structures. The HOMO-LUMO gaps of the lowest-energy structures indicate that with the exception of Si₄C₇ and Si₁₂C, the ground states are of high chemical stability and have the characteristics of semiconductors. In addition, the Mulliken populations show that there is significant charge transfer from the silicon atoms to the carbon atoms.

Keywords: SiC, clusters, ground state, stability.

1. INTRODUCTION

The structures and properties of mixed silicon-carbon clusters have been the subject of great scientific interest both theoretically and experimentally over the past decades. Although carbon and silicon are in the same column (Group IV) of the periodic table of elements, their chemical and bonding properties are rather different. Carbon exhibits huge flexibility by forming either single or multiple bonds, resulting in a variety of cluster geometries [1–3]: silicon prefers single bonds and generates compact three-dimensional (3D) structures. The study of mixed silicon-carbon clusters is therefore of interest not only for producing new materials for the nanoelectronics industry, but also for understanding the nature of these clusters from a fundamental perspective.

In the past two decades, a series of mixed silicon-carbon clusters has been studied [4–8]. By using the local density approximation (LDA) method and time-dependent density functional theory (DFT), the electronic and geometrical structures of small SiₙCₙ₋ₙ (m + n ≤ 5) clusters were calculated [9,10]. Next, the geometries, electronic states and energies of medium size SiₙCₙ₋ₙ (2 ≤ n ≤ 6; m = 3–16) and Siₙ₋₉C, Siₙ₋₁₂C₂ (n = 3–8) were predicted at B3LYP/6-311G* and MP2/6-311G(d) levels [11–13]. Following the structures and stability of various isomers of (SiC)₁₂ cluster were systematically computed using the DFT at the level of BLYP [14]. Furthermore, the infrared radiation (IR) spectra calculated for their typical low-energy structures of (SiC)₁₂ cluster were presented. Subsequently, Li et al reported the carbon-rich structures of CₙSiₙ (n = 1–5) clusters using the DFT B3LYP/6-311++G(2df) method [15]. They noted that the C atoms were found to form linear (n = 2), or single-ring (n = 1, 3) or double-rings (n = 4, 5) while the Si atoms preferred to attach to the carbon rings in the form of C₂Si units. Recently, the evolution of electronic structures, charge redistributions and structural properties of SiₙCₙ₋ₙ (n + m = 10) clusters were studied by using the DFT [16]. Nazrulla et al suggested that carbon atoms were the electron rich centres, while silicon atoms were electron deficient in every alloy cluster. For larger sizes of mixed Si-C clusters, Zhu et al [17] investigated the growth patterns and electronic property of Si₁₂C₁₂ cluster-assembled materials. In addition, by using the DFT and the coupled-cluster theory, some SiₙCₙ₋ₙ (m, n ≤ 12) clusters ranging in size from Si₉C to Si₁₂C₁₂ were predicted [18]. Most recently, silicon impacts on structure, stability and aromaticity of C₂₀₋₉Si₉ heterofullerenes (n = 1–10) were studied in a density functional perspective [19]. However, the studies of the Si-rich or C-rich mixed silicon-carbon clusters are still far from complete.

In the present article, we make a detailed study of the stability and structural properties of SiₙC₁₃₋ₙ (n = 1–12) nanoclusters by using all-electron DFT. The rest of this article is arranged as follows. Section 2 presents the computational methods. In section 3, we discuss the optimized structures and electronic structures of SiₙC₁₃₋ₙ (n = 1–12) clusters. A brief summary of our results is given in section 4.

2. COMPUTATIONAL METHODS

In the calculations, the electronic exchange-correlation energy was treated under the generalized gradient approximation (GGA) with the corrected-exchange potential of the Becker exchange functional and the Lee-
Yang-Parr correlation functional (BLYP) [20, 21]. A double-numerical-polarized (DNP) basis set with unconstrained spin was chosen to carry out the electronic structure calculation. The convergence criteria of the optimization were $2 \times 10^{-3}$ eV/Å and $5 \times 10^{-3}$ Å for the energy gradient and atomic displacement, respectively. The charge density was required to converge to $1 \times 10^{-6}$ eV/Å$^3$, corresponding to a total energy convergence of $1 \times 10^{-3}$ eV. All calculations were performed using the Dmol$^3$ package [22, 23].

For the Si$_{13-n}$C$_n$ ($n = 1–12$) clusters, the initial structures were taken from pure Si$_3$ clusters with some of silicon atoms replaced by carbon atoms [24]. A number of linear and annular structures and correlated structures reported in Ref. [12, 25] were also considered. Firstly, we performed symmetry-constrained geometry optimization to search for the low-lying metastable isomers among the abundant initial structures. Next, the lower-energy configurations were identified by continuing the optimization without any symmetry restrictions. Finally, frequency analyses were performed at the same theoretical level of approximation to check whether the optimum structures found are transition states or true minima on the potential energy surfaces of the corresponding cluster systems.

3. STRUCTURES AND DISCUSSION

For Si$_{13-n}$C$_n$ ($n = 1–12$) clusters, a great number of low-energy isomers with very little difference in structure are found. Geometric sketch figures of the ground states and metastable states are shown in Fig. 1. In the equilibrium geometries of the Si$_{13-n}$C$_n$ ($n = 1–4$) clusters, silicon atoms prefer to bond at one or both end(s) of a carbon chain or ring. The lowest-energy structures of Si$_{13-n}$C$_n$ ($n = 5–10$) clusters show that carbon atoms prefer forming kernels at the centre of configuration. In the case of Si$_{11}$C$_2$ and Si$_{12}$C, however, the carbon atoms are located at surface sites.

In Fig. 1, SiC$_{12}(a)$ is a linear structure with the lowest binding energy being –79.109 eV. The metastable structure SiC$_{12}(b)$ with C$_{2v}$ symmetry is a ring, and its energy is 0.264 eV higher than that of SiC$_{12}(a)$. For the SiC$_{11}$ cluster, the most stable structure is SiC$_{11}(a)$ with D$_{5h}$ symmetry in which the silicon atoms bond at the two ends of a carbon chain. This result is in good agreement with that of Ref. [12]. The energy of SiC$_{12}(b)$, with C$_{2v}$ symmetry, is 1.107 eV higher than that of SiC$_{11}(a)$, and the carbon atoms favour forming a ring. For the SiC$_{10}$ cluster, the planar structure, SiC$_{10}(a)$ with C$_{1}$ symmetry, is the ground state, silicon atoms bond at the two ends. With all silicon atoms bonding at one end, the energies of SiC$_{10}(b)$ and SiC$_{10}(c)$ are 1.045 eV, 1.539 eV higher than that of SiC$_{10}(a)$, respectively.

It can be noted that almost all the lowest-energy configurations of the Si$_{13-n}$C$_n$ ($n = 4–12$) clusters are 3D structures. We only list three 3D-lowest-energy structures for each Si$_{13-n}$C$_n$ ($n = 4–12$) cluster.

The planar and linear structures are not list in Fig. 1 due to the fact that the structures have much higher energies than the 3D structures. For the Si$_{12}$C$_8$ cluster, the lowest energy structure is SiC$_{12}(a)$ with C$_{1}$ symmetry, silicon atoms prefer to bond at the two ends.
kernels at the structural centre. The ground state of \( \text{Si}_{13}\text{C}_n \) has a \( C_1 \) geometry with a ring of carbon atoms. \( \text{Si}_{13}\text{C}_n \) lies 0.363 eV above \( \text{Si}_{13}\text{C}_0 \) in energy. We note that there are two rings in \( \text{Si}_{13}\text{C}_n (b) \): One is made of a cycle of repeating Si-C-C-Si structures, the other one is a cycle made of Si-C pairings. The energy of \( \text{Si}_{13}\text{C}_c \) is 1.035 eV higher than that of \( \text{Si}_{13}\text{C}_a \). Next, for the \( \text{Si}_{13}\text{C}_7 \) cluster, \( \text{Si}_{13}\text{C}_7 \) is the lowest-energy structure. The planar structure \( \text{Si}_{13}\text{C}_c \) with \( C_2 \) symmetry is 0.435 eV higher than \( \text{Si}_{13}\text{C}_a \) in energy. The other \( C_2 \) (II) structure, \( \text{Si}_{13}\text{C}_c \), lies 0.563 eV above \( \text{Si}_{13}\text{C}_a \) in energy. There exist a number of isomers as stable structures in the case of six carbon atoms. For the \( \text{Si}_{13}\text{C}_6 \) cluster, \( \text{Si}_{13}\text{C}_a \) in Fig. 1 has the lowest energy. \( \text{Si}_{13}\text{C}_b \) with \( C_2 \) symmetry is 0.743 eV less stable than \( \text{Si}_{13}\text{C}_a \). The third stable isomer \( \text{Si}_{13}\text{C}_c \) is a \( C_1 \) structure with a binding energy of \(-57.328\) eV, which is 1.274 eV higher than \( \text{Si}_{13}\text{C}_a \). Subsequently, \( \text{Si}_{13}\text{C}_c \) (with \( C_1 \) symmetry) is the most stable structure with three carbon atoms bonded at the center of the structure. Another stable structure \( \text{Si}_{13}\text{C}_b \) is 0.199 eV higher than \( \text{Si}_{13}\text{C}_a \) in energy. The structure \( \text{Si}_{13}\text{C}_c \) with \( C_2 \) (II) symmetry is 0.407 eV less stable than \( \text{Si}_{13}\text{C}_a \).

\( \text{Si}_{13}\text{C}_a \) and \( \text{Si}_{13}\text{C}_b \) are two different structures with an energy difference of 0.422 eV. \( \text{Si}_{13}\text{C}_a \) has the lowest energy. \( \text{Si}_{13}\text{C}_c \) is 0.495 eV higher than \( \text{Si}_{13}\text{C}_a \) in energy. \( \text{Si}_{13}\text{C}_b \), \( \text{Si}_{13}\text{C}_b \) and \( \text{Si}_{13}\text{C}_c \) are the stable structures for the \( \text{Si}_{13}\text{C}_3 \) clusters. \( \text{Si}_{13}\text{C}_a \) is the most stable structure. The \( \text{Si}_{13}\text{C}_a \) is slightly (about 0.019 eV) higher than \( \text{Si}_{13}\text{C}_b \) in energy. \( \text{Si}_{13}\text{C}_b \) is 0.619 eV higher than \( \text{Si}_{13}\text{C}_a \) in energy. For the \( \text{Si}_{13}\text{C}_3 \) cluster, the lowest-energy structure, \( \text{Si}_{13}\text{C}_a \), lies 0.093 eV below \( \text{Si}_{13}\text{C}_b \). \( \text{Si}_{13}\text{C}_b \) is 0.101 eV higher than \( \text{Si}_{13}\text{C}_a \) in energy. For the \( \text{Si}_{13}\text{C}_3 \) cluster, \( \text{Si}_{13}\text{C}_a \) is obtained as the ground state, which agrees with the structures proposed by Li et al. [25]. \( \text{Si}_{13}\text{C}_b \) and \( \text{Si}_{13}\text{C}_c \) are 0.163 eV, 0.834 eV less stable than \( \text{Si}_{13}\text{C}_a \), respectively. It is found that carbon atoms prefer the surface sites to the center sites in the ground states of \( \text{Si}_{13}\text{C}_2 \) and \( \text{Si}_{13}\text{C}_3 \).

\[ E_{\text{be}} = [E_{\text{ss}} - nE_{\text{e}} - (13-n)E_{\text{i}}]/13, \]

where \( E_{\text{ss}}, E_{\text{e}}, \) and \( E_{\text{i}} \) are the energies of isolated Si and C atoms and of the \( \text{Si}_{13}\text{C}_{13-n} \) cluster, respectively. The binding energy per atom versus the number of silicon atoms in \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters is shown in Fig. 2. It is found that the stability of \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters increases as the number of carbon atoms increases.

A vibrational frequency calculation is important for predicting structural stability. To determine the ground state of \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters, we chose at least five configurations with low binding energies and calculated the corresponding vibrational frequencies.

**Table 1.** Vibration frequencies of \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters

<table>
<thead>
<tr>
<th>No</th>
<th>( v ), ( \text{cm}^{-1} )</th>
<th>( I ), ( \text{km/mol} )</th>
<th>No</th>
<th>( v ), ( \text{cm}^{-1} )</th>
<th>( I ), ( \text{km/mol} )</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>417.6</td>
<td>0.00</td>
<td>7</td>
<td>55.2</td>
<td>0.16</td>
</tr>
<tr>
<td>2</td>
<td>2169.3</td>
<td>911.06</td>
<td>8</td>
<td>1736.6</td>
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<tr>
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<td>1.61</td>
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<td>0.21</td>
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<tr>
<td>4</td>
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<td>10</td>
<td>1066.7</td>
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</tr>
<tr>
<td>5</td>
<td>62.9</td>
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<td>11</td>
<td>40.0</td>
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</tr>
<tr>
<td>6</td>
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<td>12</td>
<td>950.0</td>
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<tr>
<td>7</td>
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<td></td>
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<td>10</td>
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<td>9.99</td>
<td></td>
<td>697.5</td>
<td>25.45</td>
</tr>
</tbody>
</table>

In Table 1, the lowest vibrational frequencies (\( \text{cm}^{-1} \)) and the highest infrared spectral (IR) intensities (\( \text{km/mol} \)) of the ground states for \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters are listed, the km in the IR intensity represents kilometer. It can be clearly seen that the ground states obtained here are actually equilibrium states without imaginary frequencies.

The HOMO-LUMO gaps of the lowest-energy structures versus the number of silicon atoms in the binary clusters are plotted in Fig. 3. It is found that the HOMO-LUMO gaps of the ground states range from about 0.422 to 1.716 eV, indicating both high chemical stability and semi-conductivity, except for the cases of \( \text{Si}_6\text{C}_7 \) and \( \text{Si}_{13}\text{C}_3 \).

![Fig. 2. Binding energy per atom (in eV) for \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters versus the number of silicon atoms in \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) the clusters](image)

In order to study the stability of \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters, we have calculated the binding energies of all the lowest-energy structures obtained here. The binding energy is defined as

![Fig. 3. HOMO-LUMO gap (in eV) versus the number of silicon atoms in \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) clusters](image)

We plot the HOMO of the lowest-energy structures of \( \text{Si}_{13}\text{C}_{13-n} \) \( (n = 1 – 12) \) in Fig. 4. It clearly shows that the frontier molecular orbitals are mainly accumulating in silicon, which results from the fact that the majority of Si atoms exhibit small coordination number and the
unsaturated Si atoms apparently show great chemical reactivity. The geometry and stability of the clusters are closely related to the bonding features and charge distributions. Analysis of the Mulliken population shows significant charge transfer from silicon to carbon. It is found that in the ground states of Si₆C₁₃₋₉ (n = 8, 9, 11, 12), most carbon atoms gain charge whereas the silicon atoms lose charge and a few silicon atoms located on the edge of the structures acquire negative charges.

![Fig. 4. The HOMO of the Si₆C₁₃₋₉ clusters (n = 1–12). The isodensity surfaces correspond to 0.030 e/a.u., where e represents electron](image)

4. CONCLUSIONS

Geometries, binding energies and electronic structures of Si₆C₁₃₋₉ (n = 1–12) clusters have been investigated using all-electron DFT. As the number of silicon atoms increases, the lowest-energy structures transform from planar structures (ring or chain) to 3D structures. We find that in the equilibrium geometries of the Si₆C₁₃₋₉ (n = 1–4) clusters, silicon atoms prefer to bond at one or two end(s) of the C chain or ring and the lowest-energy structures are all planar structures except for the case of Si₆C₈. Moreover, the lowest-energy configurations of Si₆C₁₃₋₉ (n = 4–12) clusters are all 3D structures. The most stable configurations of the Si₆C₁₃₋₉ (n = 5–10) clusters show that carbon atoms preferentially take up positions in the centre of the structures, whereas for the Si₆C₇ and Si₆C₈ clusters, carbon atoms prefer locating at the surface sites. Based on the calculation of the HOMO-LUMO gaps of the ground states, it is found that except for Si₆C₇ and Si₆C₈, the lowest-energy structures of Si₆C₁₃₋₉ (n = 1–12) have high chemical stability and semi-conductivity. Analysis of the Mulliken population shows that significant charge transfer takes place from the silicon atoms to the carbon atoms.

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REFERENCES


