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# Structure and stability of a silicon cluster on sequential doping with carbon atoms



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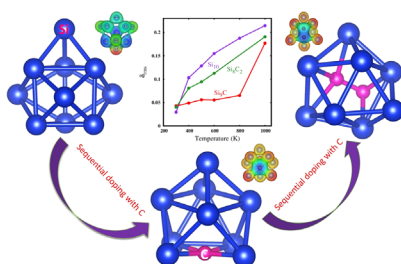
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## HIGHLIGHTS

- A well-known silicon cluster (Si<sub>10</sub>) is doped sequentially with carbon atoms.
- Carbon atoms are the electron rich centres in SiC alloy clusters.
- Silicon atoms are electron deficient in every SiC alloy clusters.
- The carbon atoms tend to aggregate together with silicon atoms surrounding them.
- Doping has implications on thermo-dynamic stability of the clusters.

## GRAPHICAL ABSTRACT



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## ABSTRACT

SiC is a highly stable material in bulk. On the other hand, alloys of silicon and carbon at nanoscale length are interesting from both technological as well fundamental view point and are being currently synthesized by various experimental groups (Truong et. al., 2015 [26]). In the present work, we identify a well-known silicon cluster viz., Si<sub>10</sub> and dope it sequentially with carbon atoms. The evolution of electronic structure (spin state and the structural properties) on doping, the charge redistribution and structural properties are analyzed. It is interesting to note that the ground state SiC clusters prefer to be in the lowest spin state. Further, it is seen that carbon atoms are the electron rich centres while silicon atoms are electron deficient in every SiC alloy cluster. The carbon–carbon bond lengths in alloy clusters are equivalent to those seen in fullerene molecules. Interestingly, the carbon atoms tend to aggregate together with silicon atoms surrounding them by donating the charge. As a consequence, very few Si–Si bonds are noted with increasing concentrations of C atoms in a SiC alloy. Physical and chemical stability of doped clusters is studied by carrying out finite temperature behaviour and adsorbing O<sub>2</sub> molecule on Si<sub>9</sub>C and Si<sub>8</sub>C<sub>2</sub> clusters, respectively.

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## 1. Introduction

Semiconductor industries have long relied on materials containing group IV elements such as silicon (Si) and germanium (Ge).

For a wide range of applications these materials have been extensively used and fabricated in both bulk and micrometre thin films. Miniaturization of electronics warrants scaling down the size of the source material to the level of nanoscale and sub-nanoscale. Due to an increase in the surface-to-volume ratio, as we scale down the size of the material, the properties of these materials become interesting and different from those of bulk. Some unique properties of interest are higher catalytic activity, better response

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properties, higher than bulk melting temperatures and so on. This size sensitivity of various properties makes it interesting and thereby motivating the researchers to simulate their behaviour using theoretical ideas. It is also now possible to synthesize these materials at sub-nanoscale and researchers have been using various techniques to synthesize these clusters experimentally and further correlate their properties using complementary theoretical studies. Interestingly, when these clusters are composed of more than one type of chemical element it is possible to alter and convincingly tune their chemical, electronic, optical and magnetic properties.

In that context, silicon clusters have been studied extensively and their properties thoroughly analyzed [1–15]. Structures of Si clusters in gas phase are studied by Lyon *et al.*, and Fielicke *et al.* These research groups have applied tuneable IR–UV two colour ionization scheme for obtaining and analyzing their vibrational spectra. Their studies reveal that small and medium sized silicon nanoclusters favour only 3-d structures. Hence, due to the absence of dangling bonds within them they are chemically non-reactive.

This problem can be overcome by doping Si clusters [16–25] with metals or by passivation of the surface. Doping Si clusters is understood to result in novel chemical, electronic, optical and magnetic properties. Doping of Si clusters with transitional metals, results in *d*-orbital occupation leading to structures with specific optical properties. This was demonstrated by Gruene *et al.* [23] where vanadium doped Si clusters lead to clusters with tuned optical properties. In another report, Ngan *et al.* [21] suggest that doping vanadium and copper into Si clusters can alter the cluster geometry, spectra and hence optical properties.

Interestingly, another element belong to group IV elements, viz., carbon in contrast to Si exhibits flexible bonding characteristics with different *sp* hybridization characteristics. As a consequence, clusters based on carbon exhibit different allotropes ranging from chains, rings, cages, tubes and sheets at nanoscale length. Carbon based nanostructures in turn have a wide ranging chemical and physical properties. In bulk, an alloy made from both Si and C has been synthesized only as late as 1900. The resulting material is an exceptionally physically and chemically strong material with low density, high thermal conductivity, high thermal stability, wide gap and chemically inert material. The same material at nanoscale length is expected to be potentially important material with exceptional properties such as low density, tuneable band gap, remarkable transport properties, superconductivity at high temperature, and semi conductivity at room temperature. The above mentioned reasons make it interesting to study and analyse the chemical and physical characteristics of Si–C nanoparticles. In particular, it is interesting to study SiC nanoclusters on account of being potential building blocks for novel materials, nanoelectronics devices and even astrochemistry.

However, unlike pure  $Si_n$  [1–15] clusters, SiC clusters are not well understood. While, it is easier to synthesize both Si and C clusters experimentally, SiC clusters have only sparsely synthesized and studied using experimental methods [26–33]. Few theoretical investigations are available where SiC clusters have been analyzed for the given ratios [34]. However, the evolution of a silicon cluster on sequential doping of carbon atoms is so far unavailable in literature except on  $Si_6$  [27]. In view of the above discussion, in this present work, we attempt to understand the implications on the electronic structure and thermal stability of a small cluster of silicon ( $Si_{10}$ ) on sequential doping with carbon atoms.  $Si_{10}$  is a special cluster which is known to be stable up to 1600 K before it fragments [12]. We have doped it sequentially with carbon atoms with stoichiometry as  $Si_{10-x}C_x$  till we reach a  $C_{10}$  cluster and their electronic structure is studied from their charge density and electrostatic potential mapping. Thermal stability of undoped  $Si_{10}$  cluster and on doping with 1 and 2 carbon atoms is also studied to understand the implications on the

thermal stability of the cluster on carbon doping. This is a first such study where the thermal stability of SiC clusters is being analyzed at nanoscale length. Finally, chemical reactivity of doped clusters exhibiting wider energy gap between the occupied and unoccupied molecular orbitals is studied by adsorbing  $O_2$  molecule and the resulting analysis is presented.

## 2. Computational details

Calculations carried out in this work are performed in the framework of density functional theory (DFT), using a linear combination of Gaussian orbitals as implemented in deMon2k code [35]. All the pure and doped clusters are optimized using the Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional [36] with DZVP basis set. The choice of the basis set and functional is based on the benchmarking results of Si–Si, C–C and Si–C dimer bond lengths and vibrational frequencies. PBE–PBE functional with DZVP basis set is seen to predict the interatomic bond lengths and vibrational frequencies closer to the experimentally observed values [see Supplementary Table 1]. Auxiliary density functional theory [37] is used to fit the density and Gen-A2 auxiliary functions are added to fit the charge density [38]. The convergence of the geometries is based on gradient and displacement criteria with a threshold value of  $10^{-3}$  a.u. and the criteria for convergence of an SCF cycle was set to  $10^{-9}$ . Ground state geometry of  $Si_{10}$  is already reported to be a tetra capped trigonal prism [12] and in this work we have also optimized 10 earlier reported conformations of  $Si_{10}$  to confirm this [12,13,15]. Following, we have sequentially doped various sites with C atoms so as to have various conformations of  $Si_nC_m$  ( $n+m=10$ ) compositions. It is important to note that some of the reports have highlighted a possibility of triplet spin state within SiC clusters [27]. Hence, to evaluate the possibility of a triplet ground state conformation, we have carried out geometry optimizations on all the clusters with both lowest spin state (i.e.  $S=1$ ) as well as triplet spin state ( $S=3$ ). The low lying conformations for each composition are identified by computing harmonic vibrational frequencies for each potential local minima. Conformations with all real frequencies are taken to be local minima. For the sake of better understanding we have denoted the ground state geometry for each composition as  $Si_nC_m$ -GS. Few representative high energy conformations are denoted by  $Si_nC_{m-1}$ ,  $Si_nC_{m-2}$ , and  $Si_nC_{m-3}$  etc. Thus  $Si_{10}$  high energy conformations are denoted as  $Si_{10-1}$ ,  $Si_{10-2}$  etc.

The optimized, lowest energy conformation of  $Si_{10}$ ,  $Si_9C_1$ ,  $Si_8C_2$  clusters are chosen as the starting conformation for all of the molecular dynamical (MD) simulations. The finite temperature simulation for each cluster is carried out implementing *ab initio* Born–Oppenheimer molecular dynamics (BOMD) using the same exchange–correlation functionals and basis set described above. The simulations are carried out between 200 K and 1000 K. At each temperature, the cluster is equilibrated for a time period of 10 ps followed by a simulation time of 40 ps. The temperature of the cluster is maintained using Berendsen’s thermostat ( $\tau=0.5$  ps). The nuclear positions are updated using a velocity Verlet algorithm with a time step of 1 fs. The atomic positions and bond length fluctuations of atoms are analyzed using traditional parameters such as root mean square bond length fluctuations  $\delta_{rms}$  and the mean square ionic displacements (MSDs). The  $\delta_{rms}$  is defined as:

$$\delta_{rms} = \frac{2}{N(N-1)} \sum_{kj} \sqrt{\frac{\langle R_{ij}^2 \rangle_t - \langle R_{ij} \rangle_t^2}{\langle R_{ij} \rangle_t}}$$

where  $N$  is the number of particles in the system,  $r_{ij}$  is the distance between the  $i$ th and  $j$ th particle in the system and  $\langle \dots \rangle_t$  denotes a time average over the entire trajectory.

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