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Stuffed fullerene structures for medium-sized silicon clusters

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Abstract. The structural properties of medium-sized silicon clusters (Si_{40}, Si_{45} and Si_{50}) have been studied using an unbiased global genetic algorithm search incorporated with a tight-binding model, followed by gradient-corrected density functional calculations. Stuffed fullerene cages are obtained as energetically favorite structures. The stuffing/cage ratio (m/n for $Si_m@Si_n$) can be understood by a space filling picture. The present results, along with our recent works on Si_N ($N = 27-39$) clusters [20], suggest that stuffed fullerene cages are the preferred structural growth pattern of medium-sized silicon clusters.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 61.48.+c Fullerenes and fullerene-related materials

As the bridge between small clusters and nanocrystallines (quantum dots), the medium-sized Si_N ($N \simeq 20-100$) clusters have attracted great attentions [1–20]. Ionic mobility experiments of the medium-sized Si_N clusters reveals a structural transition from prolate shapes to spherical-like ones around $N = 25-30$ [1]. Above the transition size, most of the cluster properties such as binding energies [2,3], ionization potentials [4], photoelectron spectra [5], and chemical reactivity [6] show smooth size-dependent behaviors. These experimental results imply that the structures of the medium-sized silicon clusters with $N \geq 30$ may follow the same growth pattern and the addition of one more atom will not induce dramatic structural reconstruction of the clusters.

Because of the existence of numerous structural isomers on the potential energy surface (PES), several global optimization methods such as genetic algorithm [7], basin-hopping technique [8], "big bang" method [9], have been employed for the medium-sized Si_N clusters with $N \leq 27$. Usually, the PES of clusters during the global optimization was approximated by either empirical potentials [8] or semiempirical tight-binding models [7,9], whereas the obtained structures can be further optimized by high-level density functional theory (DFT) calculations.

On analogy to the fullerene cages of carbon clusters, silicon fullerene cages have been considered for medium-sized Si_N cluster ($N = 20-70$, in particular, at Si_{60}) [15–19]. All these studies show that empty silicon fullerene cages are unstable due to the lack of sp^2 hybridization of valence orbitals for silicon. To stabilize the silicon fullerene cage, some additional atoms stuffing inside the cage are needed to saturate the dangling bonds of the silicon fullerene surface via sp^3 hybridization. Based on this idea, some "hand-made" stuffed fullerene cages have been previously constructed for the medium-sized silicon clusters (e.g., Si_{33}, Si_{36}, Si_{39} and Si_{45}) [10–14]. However, there was no unbiased global optimization of these Si_N ($N \geq 30$) clusters to support the guess of stuffed fullerenes cages until our recent work [20]. Combining the genetic algorithm global search and an biased basin-hopping optimization, stuffed-fullerene cages were obtained as energetic favorable structures for Si_N ($N = 27-39$) [20]. An empirical rule was also proposed to estimate the ratio of "stuffing/cage" combination. To further validate the stuffed-fullerene structural pattern, it is critical to study the larger Si_N clusters with $N \geq 40$ in an unbiased global search. In this paper, we performed the genetic algorithm optimization to determine the global minimum structures of medium-sized Si_N ($N = 40, 45, 50$) clusters, and our results on the other silicon clusters up to Si_{80} will be reported in the furthercoming publications.

The structures of silicon clusters were globally optimized using an unbiased genetic algorithm (GA) [21,22] coupled with a nonorthogonal tight-binding (NTB) model [23]. At the beginning, a number of configurations on the PES were randomly generated as the initial population. Then any two individuals in this population can be chosen as parents to generate a child cluster via a "cut and splice" crossover operation [21]. With a possibility of $P_{mu} = 30\%$, mutation operation is applied to the configurations of child clusters. Then the child cluster is relaxed using BFGS numerical minimization [24], and the locally stable child is selected to replace its parents if it

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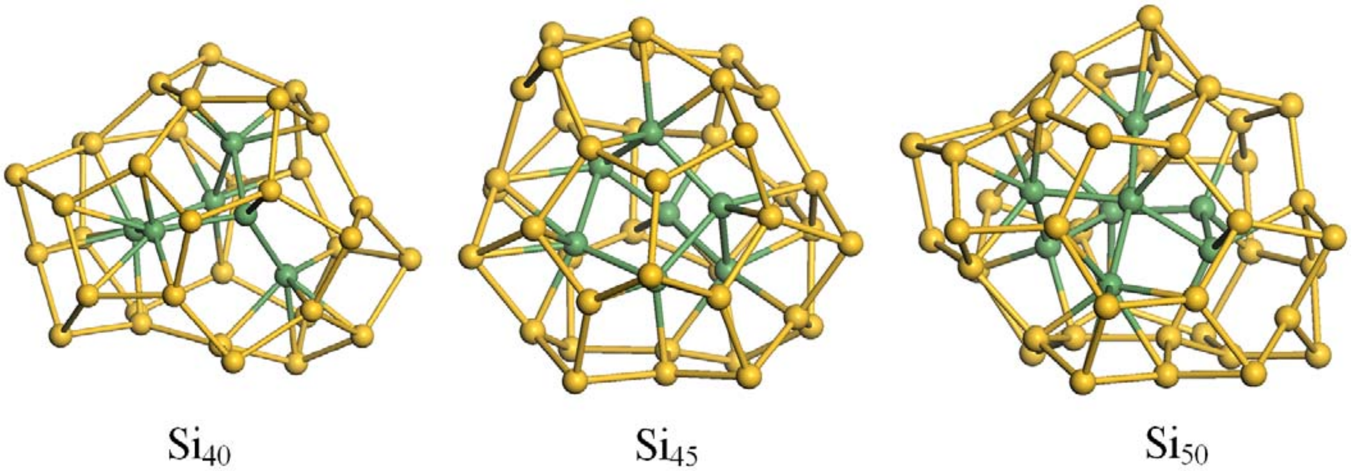

Fig. 1. Global minima structures of Si_N ($n = 40, 45, 50$) clusters. The core atoms in the fullerene cages are highlighted by green color. The stuffed fullerene cages for Si_{40}, Si_{45} and Si_{50} can be identified as $\mathrm{Si}_6@\mathrm{Si}_{34}$, $\mathrm{Si}_7@\mathrm{Si}_{38}$, and $\mathrm{Si}_8@\mathrm{Si}_{42}$, respectively. A color version of the figure is available in electronic form at `http://www.eurphysj.org`.

has lower energy. To ensure the global minimum in the PES, we repeat GA iterations up to 40 000 steps. The PES of silicon clusters is described by a NTB total energy model by Menon and Subbaswamy [23], which has successfully described the structures and binding energies of small Si_N clusters ($N \leq 10$) [23] and has been applied to Si_{45} cluster [13]. An all-electron density functional DMol^3 program [25] with double numerical plus d basis sets and PBE exchange-correlation functional [26] was used to further optimize the structures from NTB calculations.

The lowest-energy structures for Si_{40}, Si_{45} and Si_{50} clusters obtained by unbiased GA search are presented in Figure 1. All of those medium-sized silicon clusters belong to the stuffed fullerene cages and can be characterized as $\mathrm{Si}_6@\mathrm{Si}_{34}$, $\mathrm{Si}_7@\mathrm{Si}_{38}$, and $\mathrm{Si}_8@\mathrm{Si}_{42}$, respectively. In previous works, "hand-made" stuffed fullerene structures have been constructed for Si_{45} cluster by placing a bulk-like core of five silicon atoms inside a Si_{40} fullerene cage [10–12]. By DFT local minimizations, we compare the binding energies of our global minimum structure as $\mathrm{Si}_7@\mathrm{Si}_{38}$ in Figure 1 with a previous proposed $\mathrm{Si}_5@\mathrm{Si}_{40}$ structure [12]. The total binding energy of the present $\mathrm{Si}_7@\mathrm{Si}_{38}$ structure is lower than that of the previous $\mathrm{Si}_5@\mathrm{Si}_{40}$ structure [12] by about 1.8 eV. This result is similar to our previous finding for those smaller Si_N ($N = 27-39$) [20] that the bulk-like core is not energetically favorable for stuffing the medium-sized fullerene silicon cages. To minimize the total energy, the inner silicon atoms will adjust their positions to accommodate the configuration of the outer cage and to saturate the surface dangling bonds. But we can still find some inner silicon atoms exhibit tetragonal coordination with sp^3 hybridization, implying that the stuffed fullerene structures might be embryo of nanocrystalline at very early stage. Furthermore, we have evaluated the average coordination number (CN) of the structures in Figure 1. Using a 2.6 Å cutoff for Si-Si bond length (the next nearest interatomic distance of silicon in β-tin phase is 2.585 Å), the CN of these three clusters is all around 3.9, close to the four-fold coordination environment of diamond phase.

In our recent studies of Si_N ($N = 27-39$) [20], an empirical rule for the stuffing/cage ratio m/n of a stuffed fullerene cage $\mathrm{Si}_m@\mathrm{Si}_n$ was proposed based on the results of GA global optimizations [20]. For a fullerene cage with $n = 26+2x$ atoms, the upper limit for the number of stuffing atoms m is $3+x$. According to this rule, the maximum number of stuffing atoms in Si_{34}, Si_{38} and Si_{42} is 7, 9, and 11 respectively, whereas our GA global optimization results are $m = 6, 7$, and 8. Thus, the present GA optimizations for Si_N with $N \geq 40$ further confirmed this empirical rule of stuffing. More interestingly, we find that the stuffing/cage ratio can be estimated from a simple space-filling model. Choosing several representative high-symmetric carbon fullerenes such as $\mathrm{C}_{26}(D_{3h})$, $\mathrm{C}_{36}(D_{6h})$, $\mathrm{C}_{50}(D_{5h})$, and $\mathrm{C}_{60}(I_h)$, we can fit a relation between number of atoms n and surface area of the fullerene cage by counting the number of pentagonal and hexagonal rings on the cage. Assuming a spherical shape of the clusters and using the atomic volume in bulk diamond phase, the number m of the atoms stuffed inside a spherical-like fullerene cage with n atoms (in the range of $n = 26-60$) can be expressed by a simple function as:

$$m \simeq 0.00515n^2 + 0.03071n - 1.5525. \qquad (1)$$

For $n = 34, 38, 40$, equation (1) predicts $m = 5.4$, 7.0, 8.8 respectively, very close to our GA results as $m = 6, 7, 8$. Moreover, it is noteworthy that the above estimation is based on the assumption of spherical cage. In some situations, the shape of medium-sized silicon clusters may deform from sphere and become oblate-like or prolate-like. Consequently, the inner space of the cage for stuffing will be reduce. Therefore, equation (1) can be used as the estimation for the optimal stuffing/cage ratio for near-sphere fullerene cages and also serve as an upper limit for the clusters with other shapes (oblate or prolate).

We now discuss the binding energies of these stuffed fullerene cages as function of cluster size N. In previous experiments [2,3], it was found that the binding energies E_b per atom of Si_N clusters ($N \geq 25$) can be described by a simple $N^{-1/3}$ dependence as

$$E_b(N) = E_b(\infty) - cN^{-1/3}, \tag{2}$$

indicating compact spherical-like geometries. For the medium-sized range of $25 \leq N \leq 70$, the coefficient $c = 2.33 \pm 0.03$ eV [3] is obtained from collision induced dissociation experiments [2]. From our present DFT calculations with PBE functional, the binding energies for Si_{40}, Si_{45} and Si_{50} are obtained as and 3.84, 3.88, and 3.88 eV/atom, respectively, in satisfactory agreement with experimental estimations as 3.95, 3.97 and 4.00 eV/atom from equation (2).

In summary, based on the unbiased GA global optimizations, we have shown that the stuffed fullerene cages are the generic structural pattern for the medium-sized silicon clusters up to at least 50 atoms. The ratio of stuffing/cage of the stuffed fullerene can be explained by a simple space-filling model. The theoretical binding energies of the clusters agree well with experiments. Due to the extreme complicity of the PES of the medium-sized clusters and the limitation of numerical local minimization used the GA optimizations, it should be noted that the present GA optimization may not be able to locate the "best" stuffed fullerene structures even through it is a global minimization algorithm. However, guided by the unbiased GA results and the empirical rule of stuffing/cage ratio, one can construct some "hand-made" stuffed fullerene cages and locally optimize their structures to obtain the optimal stuffed cages. The computational work in this direction is now under way.

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