Silicon Clusters

Motif Transition in Growth Patterns of Small to Medium-Sized Silicon Clusters**

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Semiconductor clusters are a special class of matter with sizes inbetween single atoms and semiconductor quantum dots.[1] Small to medium-sized semiconductor clusters have received considerable attention since the 1980s, largely because of their potential relevance to and applications in the silicon-based nanoelectronics industry. It is known that geometric structures of semiconductor clusters generally bear little resemblance to those of their bulk counterparts.[2–6] In particular, the Si_6 tetragonal bipyramid, Si_7 pentagonal bipyramid, and Si_{10} tetracapped trigonal prism are known as magic-number clusters because, on collision or laser vaporization, medium-sized clusters dissociate mainly by loss of these Si_6, Si_7, or Si_{10} species.[7,8] Moreover, ion mobility measurement on cluster cations Si_n^+ has revealed a remarkable growth-pattern transition from "sausagelike" prolate clusters to near-spherical ones over the size range of $25 \leq n \leq 30$.[9] Despite major advances in experimental characterization of semiconductor clusters in the past decade,[5–10] the detailed morphology of silicon clusters with sizes larger than ten atoms still cannot be inferred directly from experiments. Hence, structural determination of small to medium-sized

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semiconductor clusters has heavily hinged on quantum-mechanical calculations in conjunction with the current global search techniques.[11–18] To date, the global-minimum structures of small neutral silicon clusters Si_n up to $n = 12$ have been well established on the basis of ab initio calculations. Identification of true global-minimum structures for clusters beyond $n = 12$ remains a subject of current research.[15–17]

Previous unbiased global searches using the genetic algorithm (GA) in conjunction with semiempirical tight-binding and first-principles density functional theory (DFT) have revealed a number of generic features in the growth pattern of small to medium-sized silicon clusters. For example, in the size range of $12 \le n \le 18$, Ho et al. reported that the clusters are mostly built up with the tricapped trigonal prism (TTP) Si_9 motif.[11] Later, Jackson et al. performed unbiased searches using single-parent GA as well as the big-bang method[12,17] and revealed a motif transition, starting at $n = 19$, from TTP Si_9 to a complex of the Si_6 tetragonal bipyramid and Si_6 sixfold puckered ring. The former Si_6 subunit is the magic-number cluster, whereas the latter is a part of the "adamantane" unit, a fragment of bulk diamond.[2,5,12,17] Hereafter, we refer to the complex of the Si_6 tetragonal bipyramid and Si_6 sixfold puckered ring as the six/six (Si_6/Si_6) motif. Note that for small clusters it is well known that the addition of one more atom can often cause dramatic structural reorganization. Thus, it is not surprising that abrupt structural transition can occur in the growth pattern of small to medium-sized silicon clusters. However, what is remarkable in this particular case is that the onset of bulk fragments—the Si_6 sixfold puckered ring—occurs in clusters as small as Si_{19}, at which the growth pattern undergoes a TTP-to-six/six motif transition. Here we present a new global-minimum structure of Si_{16} obtained by using a computational approach that combines the unbiased basin-hopping (BH) global optimization method[18] with first-principles DFT. Through this DFT-BH approach, we demonstrate that the TTP-to-six/six motif transition occurs at even a smaller size of lowest energy cluster, that is, Si_{16}. Furthermore, through high-level ab initio calculation (at the CCSD(T) level) and DFT calculations at the PBE1PBE level with two large basis sets, we show that the new isomeric structure is slightly more stable than all low-lying structures of Si_{16} reported to date. We also show that by keeping the six/six motif as the seed in the DFT-BH search, not only can we reproduce previously reported lowest energy structures of Si_{19}, Si_{20}, and Si_{21},[12,17] but we also find new low-lying structures of Si_{17}, Si_{18}, and Si_{22}, all built upon the six/six motif.

First, we performed an unbiased DFT-BH search for the global-minimum structures of smaller sized silicon clusters Si_n ($12 \le n \le 16$), starting with several arbitrarily selected initial structures. Despite marked differences among the initial structures, the DFT-BH search indeed gives rise to the same lowest energy isomeric structure, typically, within 1000 Monte Carlo (MC) trials. We found lowest energy structures of Si_{13} and Si_{14} identical to those reported recently by Tekin and Hartke,[15] and of Si_{12} and Si_{15} identical to those reported by Ho et al.[11] However, we also obtained a lowest energy structure of Si_{16} (Si_{16a}) that differs from that reported (Si_{16b})[11] (see Figure 1); the latter has a TTP motif. Note that in the

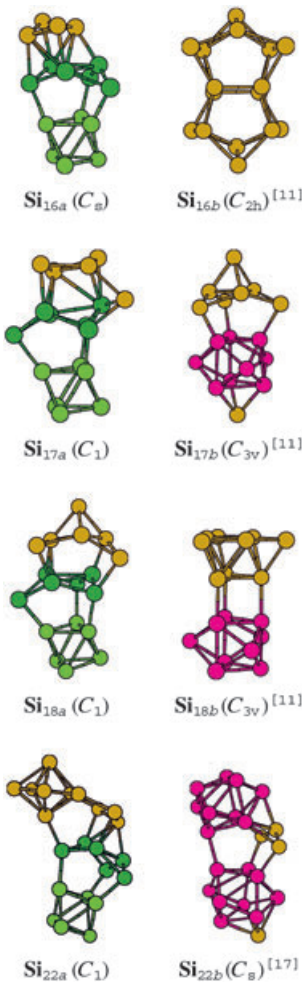

Figure 1. Lowest energy and low-lying isomers predicted in this work (left column) and those reported previously (right column).[11,17] The Si_6 tetragonal bipyramid and the Si_6 sixfold puckered ring structural subunits (i.e, the six/six (Si_6/Si_6) structural motif) are highlighted in light green and dark green, respectively, and the Si_9 tricapped trigonal prism (TTP) motif is highlighted in pink.

DFT-BH searches we selected two types of GGA exchange-correlation functional (BLYP and PBE, see Methods). Independent of the functional selected, the unbiased searches yield the identical global-minimum structure Si_{16a}.

Next, we reoptimized the Si_{16a} and Si_{16b} structures using all-electron DFT with a modest basis set, namely, B3LYP/6-311G(2d) and PBE1PBE/6-311G(2d) implemented in the Gaussian 03 code.[19] Again, both optimizations indicate that Si_{16a} is more stable than Si_{16b}. Finally, to provide more convincing evidence that the newly obtained isomer Si_{16a} is the true global minimum, we also calculated the single-point energy of Si_{16a} and Si_{16b} using a high-level ab initio molecular orbital theory with a modest basis set (CCSD(T)/cc-PVDZ), as well as using DFT (PBE1PBE) with two large basis sets (6-311G(3df) and cc-PVTZ). All calculations are based on the optimized isomeric structures at the PBE1PBE/6-311G(2d) level/basis set. The calculated total energies, including zero-point energy corrections (see Supporting Information) are listed in Table 1. All results show that the newly obtained

Table 1: Total energies [Hartree] of the lowest energy (Si_{16a}) and low-lying (Si_{16b}) isomers of Si_{16}. The binding energies per atom [eV/atom] are shown in parentheses.[a]

Basis set	Si_{16a}	Si_{16b}
B3LYP/6-311G(2d)	−4632.2049 (3.230)	−4632.2041 (3.228)
PBE1PBE/6-311G(2d)	−4630.1482 (3.631)	−4630.1430 (3.622)
CCSD(T)/cc-PVDZ	−4624.4528	−4624.4513
PBE1PBE/6-311G(3df)	−4630.2044	−4630.1984
PBE1PBE/cc-PVTZ	−4630.2355	−4630.2341

[a] The single-point energy calculations at CCSD(T) level with the cc-PVDZ basis set and DFT (PBE1PBE) level with both 6-311G(3df) and cc-PVTZ basis sets are all based on structures optimized at PBE1PBE/6-311G(2d) level/basis set. The zero-point energy correction (see Supporting Information) is included in the total energy and the binding energy per atom, calculated with the 6-311G(2d) basis set.

Table 2: Total energies [Hartree] of low-lying silicon clusters shown in Figure 1. The binding energies per atom [eV/atom] are shown in parentheses.[a]

Si_n	B3LYP/6-311G(2d)	PBE1PBE/6-311G(2d)
Si_{17a}	−4921.7345 (3.256)	−4919.5471 (3.655)
Si_{17b}	−4921.7214 (3.235)	−4919.5443 (3.650)
Si_{18a}	−5211.2486 (3.257)	−5208.9368 (3.662)
Si_{18b}	−5211.2267 (3.224)	−5208.9318 (3.654)
Si_{22a}	−6369.3400 (3.302)	−6366.5154 (3.707)
Si_{22b}	−6369.3235 (3.281)	−6366.5128 (3.704)

[a] The zero-point energy correction (see Supporting Information) is included in the total energy and the binding energy per atom.

isomer Si_{16a} is slightly lower in energy than Si_{16b}, that is, Si_{16a} is the leading candidate for the global minimum of Si_{16}. More interestingly, we find that Si_{16a} contains the six/six motif, which may suggest that the TTP-to-six/six motif transition may start at an even smaller size of cluster, namely, Si_{16} instead of Si_{19}.

To confirm the above speculation, we examined, through unbiased DFT-BH global searches, whether the global-minimum structures of Si_{17} and Si_{18} contain the six/six motif. However, because the number of local minima increases exponentially with cluster size, an unbiased first-principles BH global search becomes increasingly demanding of CPU time for larger clusters (which also have many more electrons). In fact, even though the same lowest-energy structure of Si_{16} can be obtained from an unbiased DFT-BH search with less than 5000 MC trials (regardless of the initial structure), the unbiased search starts to show dependence on initial structure starting from Si_{17}, at least within a few thousand MC trials. From our previous experience of BH searches with empirical potential of silicon,[20] the number of MC trials required to locate the true global minima for some medium sized clusters may be up to the order of 10^4 or even 10^5. However, for a first-principles DFT-BH search, 10^5 MC trials would require more than one year CPU time on our 16-CPU AMD Athlon cluster.

We therefore undertook a more efficient (but biased) search—a DFT-BH search with a fixed seed—in order to examine the possibility of finding new low-lying structures of Si_{17} and Si_{18} that are built on the six/six motif. To this end, during the DFT-BH search, we kept the structural integrity of the six/six motif (the seed) while allowing the remaining silicon atoms to undergo the MC trial. Remarkably, this biased DFT-BH search (with the BLYP GGA functional) not only can reproduce the global-minimum structures of Si_{19}, Si_{20}, and Si_{21} reported previously,[12,16,17] but also can produce new low-lying isomers of Si_{17}, Si_{18}, and Si_{22} (see Si_{17a}, Si_{18a}, and Si_{22a} in Figure 1). These new isomers are appreciably lower in energy than the lowest energy isomers published previously (Si_{17b}, Si_{18b}, and Si_{22b}),[11–17] which all contain the TTP motif. We also relaxed these six isomers using all-electron DFT with modest basis sets, that is, B3LYP/6-311G(2d) and PBE1PBE/6-311G(2d).[19] Table 2 lists the calculated total energies, including zero-point energy corrections (see Supporting Information), and the binding energies per atom. These energy data show that the new low-lying isomers built on the six/six motif are indeed more stable than the isomers built on the TTP motif. The fact that the six/six motif emerges in all low-lying clusters of Si_{16}–Si_{22} suggests that the sixfold puckered ring plus magic-number cluster complex may be viewed as another type of generic structural motif in the growth pattern of small to medium-sized silicon cluster besides the well-known TTP motif. The latter emerges only in smaller silicon clusters starting from Si_{10} and ending at Si_{15}, and the TTP-to-six/six motif transition occurs at Si_{16}. Figure 2 graphically illustrates this TTP-to-six/six motif transition. In passing, we note that Jackson et al.[17] have recently shown through an unbiased search that the growth pattern for medium-sized cluster cations Si_n^+ undergoes another major structural transformation, that is, the prolate-to-spherical-like structural transformation, at $n \approx 27$. Combining our theoretical results with theirs, we conclude that in the evolution of silicon clusters from small to medium size, that is, from $n \approx 16$ to $n \approx 26$, the prolate-shaped lowest energy clusters are likely to contain a sixfold puckered ring plus magic-number cluster motif, where the magic-number cluster can be Si_6 (i.e., six/six motif) or Si_{10}. The six/ten (Si_6/Si_{10}) motif, which can be viewed as the third type of generic structural motif, starts at $n = 23$ (see Figure 2).

In summary, we have found a new global minimum of Si_{16} as well as low-lying isomers of Si_{17}, Si_{18}, and Si_{22} using a DFT-BH computational approach. These new low-lying isomers are all built on the generic six/six (Si_6/Si_6) motif, and they are lower in energy than those built on the well-known TTP Si_9 motif. We show that the TTP-to-six/six motif transition occurs at Si_{16}. Prior to the onset of the prolate-to-spherical-like growth-pattern transformation at $n \approx 27$, all prolate-shaped clusters are likely built on generic structural motifs of the sixfold puckered ring plus a magic-number cluster, where the magic-number cluster can be Si_6 or Si_{10}.[17] The six/six-to-six/ten motif transition appears to occur at $n \approx 23$. Finally, the prolate-to-spherical-like (e.g., endohedral silicon fullerenes[22]) structural transition is likely to occur at $n \approx 27$.[17]

Experimental Section

To seek lowest-energy geometric structures for small to medium-sized clusters, we adopted the basin-hopping (BH) method[18] and combined it with first-principles DFT with two types of exchange-correlation functional (BLYP and PBE). Both types of functional are

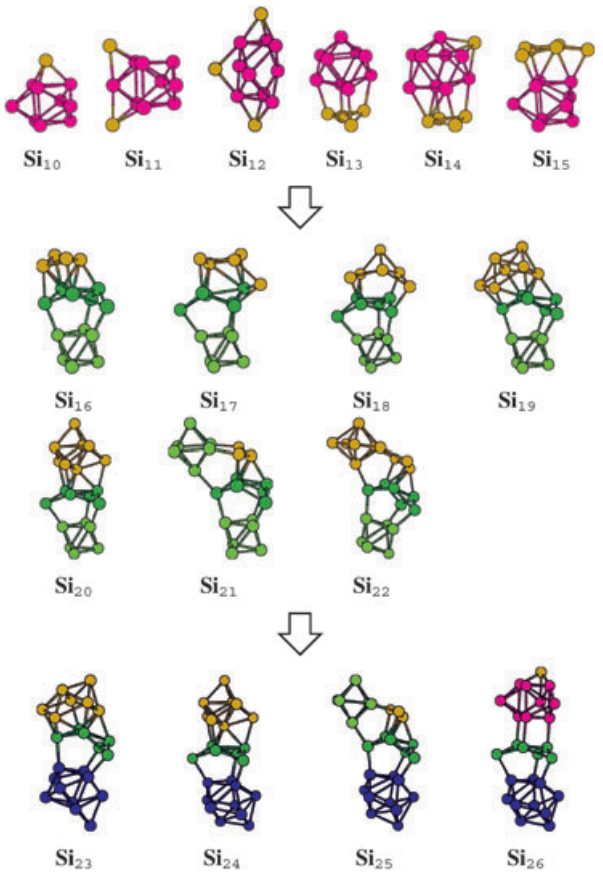

Figure 2. Lowest energy isomers (Si_{10}–Si_{15}) predicted previously,[11,15] those reported in this work (Si_{16}–Si_{18}, Si_{22}), and those (Si_{19}–Si_{21}, and Si_{23}–Si_{26}) predicted by Jackson et al.[12,17] The Si_9 TTP motif is highlighted in pink. The Si_6 tetragonal bipyramid, the Si_6 sixfold puckered ring, and the Si_{10} magic-number cluster structural subunits are highlighted in light green, dark green, and dark blue, respectively.

implemented in CPMD code.[21] The source code of CPMD is freely available to academic researchers. Therefore, we were able to merge our BH Monte Carlo code with the CMPD code. In the DFT-BH search, we used the Monte Carlo scheme to explore the potential energy surface transformed by the DFT structural optimization, i.e., we calculated the potential energy and energy gradient using subroutines for DFT energy minimization implemented in the CPMD source code. Once the lowest energy isomers were identified, all-electron DFT calculations at the B3LYP/6-311G(2d) and PBE1PBE/6-311G(2d) levels/basis set (implemented in the Gaussian 03 code[19]) were carried out to further relax the isomers (with no symmetry constraint). Harmonic vibrational analysis at the B3LYP/6-311G(2d) and PBE1PBE/6-311G(2d) levels/basis set was also performed to assure that the isomers are local minima with no imaginary frequency. Zero-point energies are reported in the Supporting Information. For Si_{16}, all-electron ab initio molecular orbital calculations at the coupled-cluster single and double substitutions (including triple excitations) CCSD(T) theory with cc-PVDZ basis set, as well as DFT (PBE1PBE) calculations with both 6-311G(3df) and cc-PVTZ basis sets,[19] were also carried out to confirm that the new isomer Si_{16a} has a lower single-point energy than the previously reported global-minimum structure Si_{16b}.

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