Structure and stability of Si$_{45}$ clusters: A generalized tight-binding molecular-dynamics approach

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We compare the relative stabilities of all the proposed low-energy isomers of the Si$_{45}$ cluster using a generalized tight-binding molecular-dynamics scheme. This technique has been used earlier to obtain good agreement with ab initio results for small silicon clusters and shown to be transferable to bulk solids. In agreement with local-density-approximation-based results, we find the lowest-energy structure to consist of two concentric shells with a highly distorted fullerene-like outer layer, and a highly coordinated inner core with a central atom. Additionally, we have found several nearly isoenergetic structures in which the inner core has no central atom. This suggests that structural transition to bulklike coordination might occur for significantly larger clusters.

I. INTRODUCTION

Elkind et al. have found that the reactivity rates for intermediate-sized silicon clusters show considerable variation with cluster size. In particular, Si$_{26}$, Si$_{33}$, Si$_{39}$, and Si$_{45}$ have been found to be least reactive. Motivated by this finding, several groups have proposed various structures as possible ground state geometries for these clusters. An underlying theme among these is the saturation of the reactive dangling bonds. Theoretical work has mostly been focused on Si$_{45}$. All the structures proposed, with the exception of that in Ref. 6, exhibit high degrees of symmetry. Also, only the structure proposed in Ref. 6 has been subjected to full geometry optimization based on first-principles methods.

The models proposed for Si$_{45}$ can be broadly categorized as follows: (1) A tetrahedrally bonded bulklike core surrounded by reconstructed bulk Si surface. This cluster can also be looked upon as a buckled Si$_{44}$ fullerene cage with one tetrahedrally coordinated atom at the center. This structure has been found to be stable under a variety of classical force-field potentials. An attractive feature of this model is that surface features closely resemble the 2×1 reconstruction of Si(111), one of the most stable reconstructions of silicon surfaces, and the structure obtained upon cleavage of the crystal. This surface passivation by reconstruction was proposed to explain the low reactivity for this cluster. (2) A 17 atom tetrahedrally connected core with an exterior consisting exclusively of five-membered rings except for the rectangular dimers. This structure has $O_h$ symmetry. This is similar to 1 with a slightly larger number of bonds for the surface atoms. This structure can also be viewed as a bulklike core surrounded by reconstructed bulk Si surface. (3) A bulklike 17 atom core surrounded by four hexagons, each capped by a single atom. This structure preserves the full $T_d$ symmetry. (4) A five atom tetrahe-
TABLE I. Cohesive energies (in eV/atom) for various optimized Si_{45} clusters in Fig. 3. The initial configurations consisted of unrelaxed fullerenes (Fig. 1) + unrelaxed cores (Fig. 2).

<table>
<thead>
<tr>
<th>Isomer label</th>
<th>Initial configuration</th>
<th>Core</th>
<th>Binding energy (eV/atom)</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a^{a} [Fig. 3(a)]</td>
<td>Si_{36}</td>
<td>Si_{19} [Fig. 2(a)]</td>
<td>4.195</td>
<td>4.44</td>
</tr>
<tr>
<td>5b^{a} [Fig. 3(b)]</td>
<td>Si_{38}</td>
<td>Si_{17} [Fig. 2(b)]</td>
<td>4.248</td>
<td>4.04</td>
</tr>
<tr>
<td>5c^{b} [Fig. 3(c)]</td>
<td>Si_{38}</td>
<td>Si_{17} [Fig. 2(c)]</td>
<td>4.240</td>
<td>4.00</td>
</tr>
<tr>
<td>5d^{b} [Fig. 3(d)]</td>
<td>Si_{40}</td>
<td>Si_{19} [Fig. 2(d)]</td>
<td>4.239</td>
<td>3.73</td>
</tr>
<tr>
<td>5e^{b} [Fig. 3(e)]</td>
<td>Si_{40}</td>
<td>Si_{19} [Fig. 2(e)]</td>
<td>4.235</td>
<td>3.69</td>
</tr>
</tbody>
</table>

^{a}See Ref. 6.
^{b}See the present work.

performed full molecular-dynamics relaxation for these clusters starting with the initial configurations, and no stochastic searches of phase space.

The structures 1 and 2 were found to be unstable, distorting to geometries with no particular symmetries. A local minimum was found near structure 3 with the full T_{d} symmetry, but with longer bond lengths for atoms with high coordination. The energy for this structure was much higher (> 6.0 eV) than all the relaxed structures obtained, indicating it to be metastable. The authors of Ref. 4 had obtained this structure by energy optimization using the conventional orthogonal tight-binding model of Tomažek and Schlüter.\(^{13}\) This model, along with other conventional orthogonal tight-binding schemes, requires an ad hoc coordination-dependent term in the energy expression to get reasonable agreement with ab initio values for cohesive energies for clusters of arbitrary sizes,\(^{13,14}\) whereas our nonorthogonal scheme is free of such a term.

The structures 4 and 5 consist of fullerenelike exteriors with core atoms saturating dangling bonds. Before considering the stability of these structures, we first discuss the fullerene components briefly. The silicon fullerenes considered in forming these structures consist of Si_{36}, Si_{38}, and Si_{40} (Fig. 1); the respective symmetries are D_{6h}, C_{3v}, and T_{d}.\(^{15}\) When subjected to molecular-dynamics relaxations, these fullerenelike structures are found to be highly unstable, distorting to considerably lower symmetry geometries. The distortions are reminiscent of tetrahedral bonding geometry widely observed for silicon systems, consistent with the pronounced tendency for silicon to form sp^{3} hybrids.\(^{16}\) The introduction of core atoms within these fullerenes is expected to have a stabilizing effect by providing the silicon atoms in the cage the opportunity to form sp^{3} hybrids without puckering. In Fig. 2 we show some of the core geometries used in filling the fullerenes to obtain various stable isomers of Si_{45} in this work.

The structure 4 proposed by the authors of Ref. 5 consists of a fullerenelike Si_{40} surrounding a tetrahedral core of five atoms [Fig. 2(d)]. In the unrelaxed state, due to the large size of Si_{40} fullerene, the bonds connecting the core atoms to the cage are too long (≈ 3 Å) and the structure is expected to relax. The authors of Ref. 5 found it to preserve the T_{d} symmetry on relaxation using their classical potentials. We, however, find this structure to be unstable, relaxing to a much lower symmetry geometry.

Structures 5a and 5b were found to be stable with the 36+9 configuration [5a, Fig. 3(a)] slightly higher in energy over the 38+7 [5b, Fig. 3(b)] configuration. The energies for these structures were much lower (by at least 5 eV) than those for 1 through 4, in agreement with Ref. 6. We also obtained 5a and 5b by a full symmetry unrestricted molecular-dynamics relaxation starting from

![Fig. 1. Unrelaxed silicon fullerenes for N=36, 38, and 40.](image1)

![Fig. 2. The core atoms used in the filling of Si fullerenes of Fig. 1.](image2)
the initial symmetric configurations [unrelaxed cores in Figs. 2(a) and 2(b), and fullerene cages for \( N=36 \) and \( N=38 \)]. The geometry 5b was the lowest in energy of all configurations considered and also was the only one that possessed any symmetry \( (C_3) \). The slight energy difference in favor of 5b over 5a is understandable in view of the higher strain encountered in containing a relatively larger core by a relatively smaller fullerene in the case of 5a. The average coordination numbers for geometries 5a and 5b were 4.44 and 4.04, respectively. We define the coordination number as ratio of the total number of bonds (within a given cutoff, 2.8 \( \text{Å} \) here) to the number

**FIG. 3.** Relaxed geometries of the low-energy isomers for \( \text{Si}_{45} \) obtained using the present molecular-dynamics scheme. The initial configurations consisted of unrelaxed fullerenes (Fig. 1) + unrelaxed cores (Fig. 2). See Table I for more details. The relaxed geometries shown are (a) 36+9 (configuration 5a), (b) 38+7 (most stable, 5b), (c) 38+7 (with no central atom, 5c), (d) 40+5 (configuration 5d), and (e) another 40+5 combination (with no central atom, 5e).
of atoms in the cluster.

The high coordination of the core atoms is reminiscent of the ground state structures of small silicon clusters with N<10. In view of this similarity, we considered the possibility that the lowest-energy geometry of Si\textsubscript{7} (pentagonal bipyramid)\textsuperscript{10,12} [Fig. 2(c)] could form a stable core for Si\textsubscript{45}. A stable geometry was obtained for this 7+38 combination on relaxation, although slightly higher in energy [5c, Fig. 3(c)]. The relaxed structure had a coordination number of 4.00 and no particular symmetry.

The relaxation of structure 4 also produced several low-energy isomers competitive in energy with the other structures considered. Interestingly, these structures had lower coordination numbers. In order to search for low-energy geometries starting with Si\textsubscript{6} and Si\textsubscript{40} combinations, we considered several distinct orientations of the tetrahedral core [Fig. 2(d)] suggested in Ref. 5 and performed relaxations by first imposing symmetry constrains and then removing them. The lowest-energy geometry for this 5+40 combination was obtained starting from an initial configuration where the four second shell atoms capped the four sides of the Si\textsubscript{10} fullerene cage that were related by T\textsubscript{d} symmetry [5d, Fig. 3(d)]. The coordination number for this geometry was 3.73. Another structure almost isoenergetic to this was obtained by using the ground state structure for Si\textsubscript{5} (compressed trigonal bipyramid, D\textsubscript{3h} symmetry)\textsuperscript{10,12} [Fig. 2(e)] as the core and performing a symmetry restricted relaxation followed by relaxation with no restrictions [5e, Fig. 3(e)]. The coordination number for this structure was 3.69. In Table I we give a summary of binding energies and average coordination numbers for these isomers.

III. DISCUSSION

The implications of these findings are intriguing. The stable low-energy isomers 5a, 5c, and 5e [Figs. 3(a), 3(c), and 3(e), respectively] contain no central atom and all these structures have highly coordinated cores. Additionally, the overall shapes are approximately spherical with hardly any symmetry. The arguments made in favor of bulklike tetrahedrally coordinated core atoms surrounded by surface atoms resembling reconstructed bulk surface, although cogent, may not be applicable to clusters of this size. The relatively large ratio of surface atoms to bulk (> 3) prevents it from being a true representative of bulk solid.

It is worth noting that the classical potentials used in optimizations for the clusters 1, 2, and 4 have not been successfully tested in the range up to N=10 where \textit{ab initio}\textsuperscript{11,12} results, readily available, predict them to be highly coordinated with low symmetries. Although a local minimum was obtained near 3, the energy was considerably higher (>6 eV). Our results agree with local-density-approximation (LDA) based results in finding the lowest-energy structure [5b, see Fig. 3(b)] to consist of two concentric shells with a highly distorted fullerene-like outer layer, and a highly coordinated inner core. We note that the GTBMD scheme, which also agrees quantitatively with \textit{ab initio} and LDA results for other size clusters, is two orders of magnitude faster than these first-principles methods.

The coordination numbers for these isomers offer some interesting insights into the preferred cluster geometry. The lowest-energy structure obtained here has an average coordination near 4 (see Table I). The gain in energy by forming increasing number of bonds is offset by an increase in the strain with increasing coordination. As evidenced in Table I, a happy compromise is obtained for structure 5b [Fig. 3(b)].

The lack of bulklike coordination for Si\textsubscript{45} raises another important and provocative issue of cluster sizes for which structural transition to bulklike coordination might be achieved. We believe this to occur for much larger sizes where the ratio of surface atoms to bulk is near unity. In particular, transformation of the core atoms to tetrahedral coordination is likely to hold the key in the investigation.

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