Distorted cage structures of Si$_n$ (n = 20, 24, 26, 28, 30, 32) clusters

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Abstract

We have performed calculations on the fullerene cage structures and the binding energies of Si_n (n = 20, 24, 26, 28, 30, 32) clusters by the full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO-MD) method. It is found that the fullerene cages are not stable, and relax into structures which are severely distorted. Except for Si_{20}, their atomic arrangement tends towards tetrahedral geometry. After the structural distortion, about two silicon atoms can still be filled into the inside spaces of the distorted cages for Si_n (n = 26–32).

1. Introduction

The truncated icosahedral cages (fullerene cages) are important structures for C_n clusters [1,2]. They have 12 pentagons on their almost spherical surfaces. Extensive investigations on the fullerene cages of the C_n clusters have been performed. It is believed that the perfect truncated icosahedral cage structures for C_{60} and C_{70} clusters are especially stable. Theoretical investigations have shown that a whole family of fullerenes can exist for carbon clusters [1]. Further probing suggests that in addition to C_{60} and C_{70}, the C_{24}, C_{28}, C_{32} and C_{50} clusters should also show varying degrees of special stability [1]. Recently, Piskoti *et al* [3] have reported that the structures with D_{6h} and D_{2d} symmetry for C_{36} cages are the most stable. Grossman *et al* [4] have provided a theoretical characterization of solid C_{36}. Each atom of the cage structures is bonded to three other atoms, thus making it a form of spherical graphite. We wondered if silicon, contiguous to carbon in the periodic table, would also form the stable icosahedral cage structure. For the Si_{60} cluster, a few reports have involved Si_{60} cage structure [6–13]. We have also investigated the cage structure of the Si_{60} cluster [14] by the full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO-MD) method [14]. Our results indicate that the truncated icosahedron has been distorted from I_h symmetry to T_h symmetry. Its final stable structure resembles a puckered ball. For other truncated icosahedra, we want to know whether they can be stable, and how they are distorted if they are unstable.

Kaxiras and Jackson have addressed the fullerene cages of Si_{20}, Si_{26} and Si_{28} in their paper [15]. In present paper, we have performed calculations on the cage structures of Si_{20-32} clusters by means of molecular dynamics simulations for the first time. Recently, Marsen and Sattler proposed a fullerene-type Si_{24}-based atomic configuration for nanowires of silicon [16]. Our investigations on the fullerene cages help us to understand the growth of the silicon nanowires on the basis of the cages.

2. Method

The FP-LMTO method [17–20] is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [21]. In this method, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centred at the nuclei and the remaining interstitial region. The electron wave functions are expanded in terms of muffin-tin orbitals [22]. The LMTOs are augmented Hankel functions, and are augmented inside the MT spheres, but not in the interstitial region [22–24]. The LMTO basis sets include s, p and d functions on all spheres. The potential and density are expressed as linear combinations of Hankel functions. The details of how the molecular dynamics method can be performed are described in references [14, 19, 20].

3. Structures and discussion

The initial configurations of Si_n ($n = 20$, 24, 26, 28, 30 and 32) are perfect fullerene cages. After relaxation, they have been distorted severely except for Si_{20}. Their initial and final configurations are shown in figure 1. The point groups, binding energies per atom and diameters of the inside spaces are shown in table 1 for these clusters.

Table 1. Point groups (S), binding energies (E_b, in eV), binding energies per atom (E_a, in eV) and diameters of inside spaces (ΦD, in Å) for the final structures and the initial cage structures of Si_{20-32} clusters.

Initial structure	20	24A	26A	28A	28C	30A	32A
S	I_h	D_{6d}	D_{3h}	T_d	D_{3h}	D_{5h}	D_{3d}
ΦD	6.9	7.2	7.5	7.6	—	7.8	8.1
Final structure	20	24B	26B	28B	28D	30B	32B
S	I_h	C_2	C_s	C_s	C_s	C_{2v}	C_2
E_b	91.69	117.35	125.19	137.64	139.56	146.26	156.94
E_a	4.59	4.89	4.82	4.92	4.98	4.88	4.90
ΦD	6.5	3.9	6.0	6.0	—	6.0	6.0

3.1. Si_{20} and Si_{24}

Theoretically, Si_{20}, the smallest silicon cluster, can exist as a fullerene cage. It is found from our calculations that the perfect cage for Si_{20} is stable, but it is 6.74 eV less stable than its ground-state structure with C_2 symmetry, which is a stack of tetracapped trigonal prisms [25]. In fact, the binding energy difference of 6.74 eV makes it difficult to find experimentally. Its configuration is shown as the last one in figure 1.

The fullerene cage of Si_{24} (D_{6d} symmetry) has two hexagons on its spherical surface, shown as 24A in figure 1. The surface atoms have threefold coordination. Structural optimization
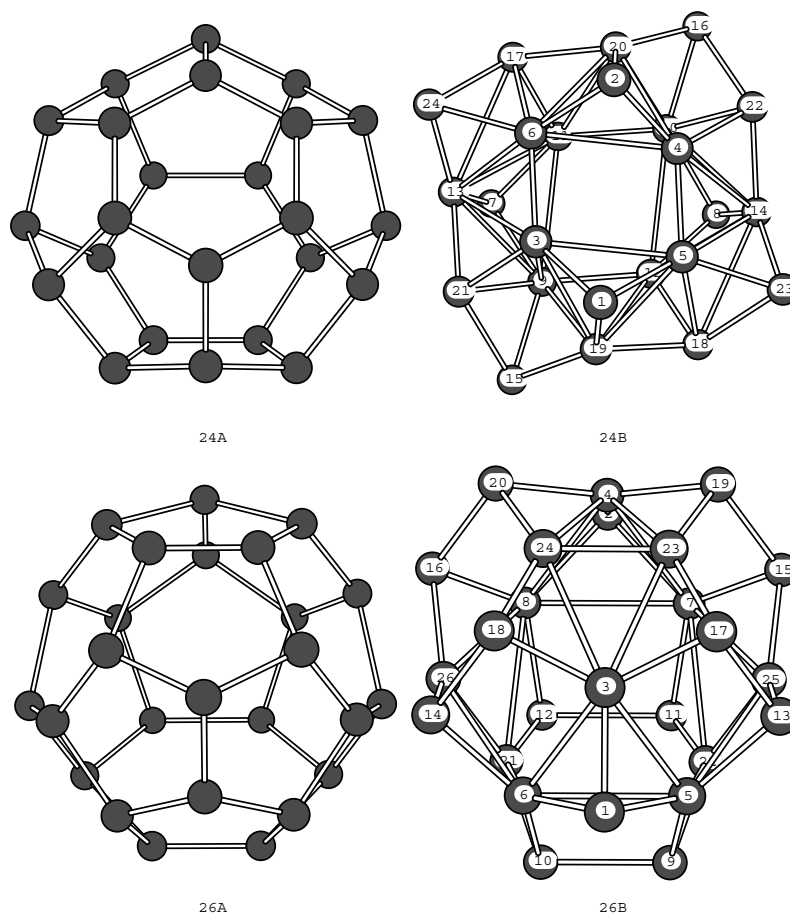
Figure 1. Initial (on the left) and final (on the right) configurations of Si$_{24-32}$ clusters. The last one (20) corresponds to the cage of the Si$_{20}$ cluster.

finds it to be unstable, and it undergoes significant distortion into a structure with less symmetry (C$_2$), shown as 24B in figure 1. Its binding energy per atom is 4.89 eV, which is obviously larger than that of Si$_{20}$. It is found from observing 24B that some atoms have moved outwards, whereas other atoms have moved inwards. After the distortion, some new bonds appear in its two hexagons, forming two rhombuses. In addition, there are many tetrahedral configurations on its surface. The atoms have at least fourfold coordination. As a result, the inside space of the cage obviously decreases. The diameter of its initial cage is about 7.5 Å, while the distance shortens to about 3.9 Å upon distortion. Therefore, it is difficult to fill interior silicon atoms into the distorted cage. But the space length of 3.9 Å indicates that the structure is not a very compact structure.

3.2. Si$_{26}$ and Si$_{28}$

The initial cage of Si$_{26}$ has D$_{3h}$ symmetry; it is shown as 26A in figure 1. The 26-atom cage cluster consists of two hemispherical domes of ten atoms joined by a ring of three dimers [15]. The dimers have a structure that closely resembles the dimer bonds on the Si(100)-(2×1) surface
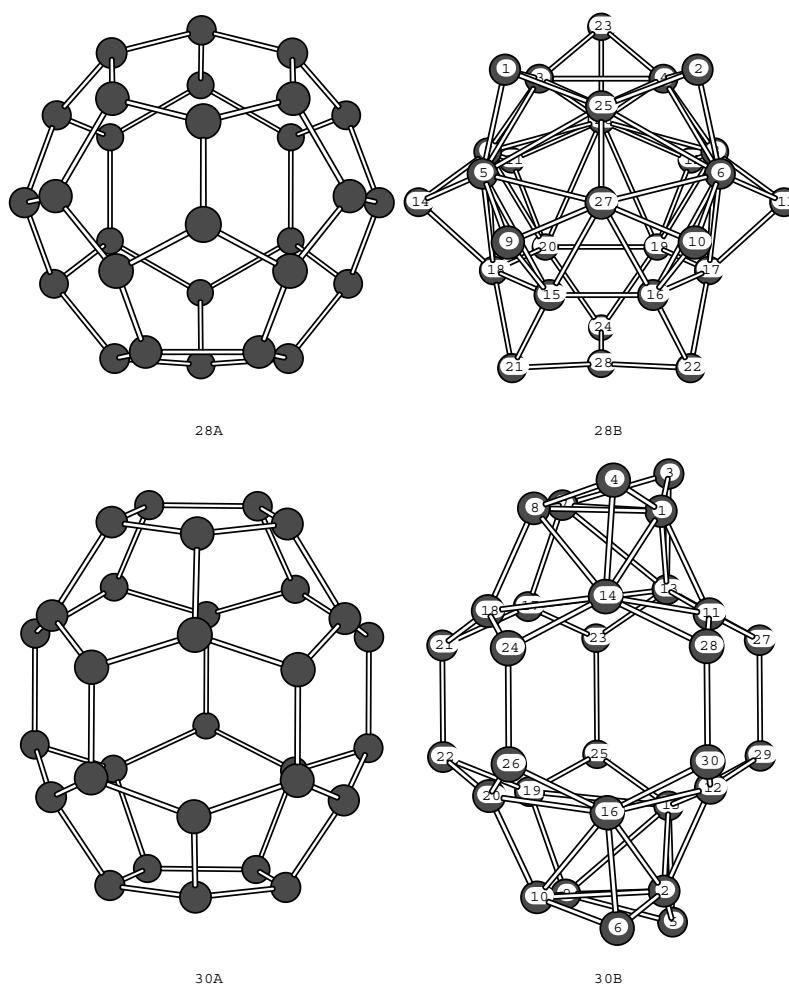
28A

28B

30A

30B

Figure 1. (Continued)

reconstruction. The 10-atom domes can be continuously deformed without any bond breaking to produce the tetracapped octahedron [15]. The tetracapped octahedron is an important structure [26]. Our calculations show that the initial cage structure with threefold coordination and 7.5 Å diameter is also unstable. Structural distortion makes its symmetry decrease to C_s. Its binding energy per atom is 4.82 eV, which is slightly less than that of Si_{24}. It is found from observing 26B that the distorted cage has similar characteristics to 24B; that is, many tetrahedra appear on its surface. But its three hexagons have different distortions from the hexagons of Si_{24}. Two of them are distorted into pentagons and trigons after two new bonds have formed, whereas the third hexagon persists. The distorted cage has an inside space with about 6.0 Å diameter. For the small silicon clusters with 2–10 atoms, the bond lengths are approximately 2.20 Å to 2.80 Å. If we were to fill interior silicon atoms into its inside up to this distance, we could still add about two more silicon atoms. Therefore, it is necessary for us to investigate the cage with two interior atoms. We insert two silicon atoms into the 26-atom perfect fullerene structure shown as 28C in figure 2 before the calculations. The 28-atom cluster has the same spherical structure as the 26-atom cluster. Structural calculations show that it is also unstable,
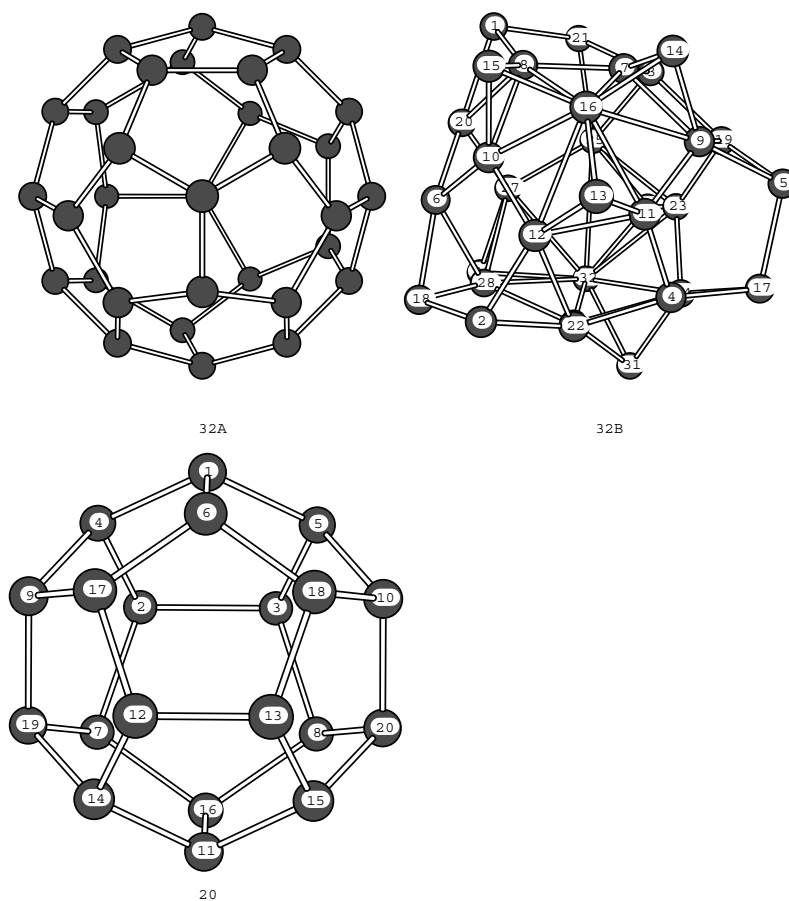
Figure 1. (Continued)

and undergoes distortion into 28D, shown in figure 2. It is found from observing 28D that it extends in the z-direction. Also, its two hexagons have been distorted into trigons, while the trigon has swollen. The distortion makes its binding energy per atom increase up to 4.98 eV, which is obviously larger than that of Si$_{26}$.

An alternative model for a 28-atom cluster is inspired by the fullerene cage shown in figure 1 (as 28A). It has perfect tetrahedral (T_d) symmetry. After structural optimization, it becomes 28B, shown in figure 1. Its four hexagons have severe distortions, forming trigonal structures. Also, it has the same characteristics as Si$_{24}$ and Si$_{26}$; that is, many tetrahedral structures appear on its surface. 28B is 1.93 eV less stable than 28D. Therefore, the perfect fullerene cage for Si$_{28}$ is unstable, and undergoes structural distortions into a much more stable distorted cage, but the distorted cage is still not as stable as the compact distorted structure with interior atoms.

3.3. Si$_{30}$ and Si$_{32}$

The 30-atom cage cluster consists of two hemispherical domes of fifteen atoms joined by five bonds, which consist of five hexagons. It is of interest to note that structural optimization makes all the pentagons distorted, but all the hexagons remain basically unchanged. In addition, our
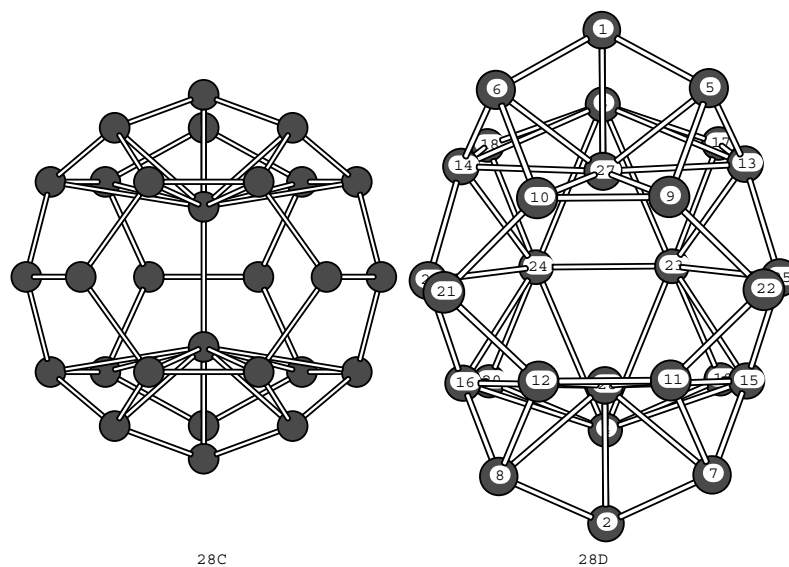
Figure 2. Initial (on the left) and final (on the right) configurations of the Si$_{28}$ cluster with two interior atoms.

investigations indicate that the five bonds joining two subunits, are strong. Their bond lengths are $d_{21-22} = 2.28$ Å, $d_{23-25} = d_{24-26} = 2.37$ Å and $d_{27-29} = d_{28-30} = 2.36$ Å, respectively.

The cage structure of Si$_{32}$ is shown as 32A in figure 1. It undergoes distortions to the much more stable structure 32B. After the distortions, all the hexagons have disappeared. They are replaced by trigons and tetrahedra. The other characteristics are similar to those of Si$_{24-30}$. We do not repeat them here.

Carbon and silicon are both tetravalent elements, but they have different properties as regards chemical bonding. Crystalline carbon exists both in the diamond phase and in the graphite phase. Experimental results show that the binding energy per atom (7.35 eV) of the former is slightly smaller than that (7.37 eV) of the latter [27, 28]. Therefore, both the diamond structure and the graphite structure can exist in solid carbon. However, crystalline silicon exists only in the diamond phase. The binding energy per atom measured experimentally is 4.63 eV, which is obviously larger than the theoretical value (3.92 eV) for a graphite structure [27, 28]. For carbon clusters, there is a tendency to form strong π-bonds, to produce chains, rings and exotic spheroidal polygonal structures. The structures of the most stable silicon clusters, apart from Si$_{3-4}$, are polyhedra or compact three-dimensional structures. They do not represent either regular or deformed sections of the corresponding crystal lattices. We have performed calculations on a piece of Si crystal network (26C), shown in figure 3. Due to the non-saturation of the edge atoms and the non-compact structure, its binding energy per atom is only 4.31 eV, which is smaller than the experimental value, 4.63 eV, for solid Si. The structural optimization finds the finite structure to be meta-stable. It would undergo severe distortion into the more stable structure 26D, shown in figure 3. The binding energy per atom in 26D is 4.55 eV. The silicon lattice can be understood as a three-dimensional network of sp^3 hybrid orbitals centred on each atom. The valence of the Si atoms is therefore saturated by bonding with four nearest neighbours located at the vertices of a regular tetrahedron. In order to reproduce such bonding, a very large number of atoms are necessary to minimize the 'edge' effects resulting from the non-saturation of the surface atoms [29]. Therefore, in the silicon clusters with finite numbers
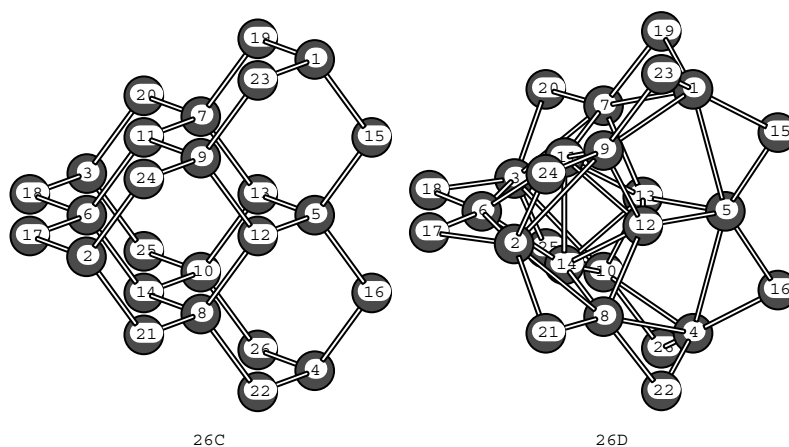
Figure 3. A piece of diamond structure with 26 atoms (on the left) and its distorted structure (on the right).

of atoms, the structures corresponding to the fullerene cages analogous to graphite sheets, or adamantane cages (a piece of the bulk diamond structure), are not the most stable. Starting with such initial structure, the molecular dynamics calculations certainly result in structural distortion due to the sp^3-hybridization-driven buckling. The distortion makes some atoms fourfold coordinated, and leads to a decrease in the number of dangling bonds. When some silicon atoms are added to the interior of the fullerene cages to form the structures resembling those discussed in references [27,31], they become more stable because the interior atoms have a high coordination number and saturate some of the dangling bonds on the cage surfaces [31]. This is in agreement with our calculated results, such as the structures 28C and 28D shown in figure 2. It is natural that the perfect fullerene cages with threefold coordination are stable for carbon, but not for silicon. However, the distorted cages are stable for silicon. Specifically, it appears that clusters of prolate shape are prevalent for sizes up to 24, whereas for larger sizes, more spherical oblate shapes dominate [32]. The distorted cages just represent one type of spherical shape.

4. Summary

We have performed calculations on the structures and energies of Si_{20-32} fullerene cages by using the full-potential linear-muffin-tin-orbital molecular dynamics (FP-LMTO-MD) method. Our calculated results suggest that they are not stable, and relax into severely distorted structures, except for Si_{20}. After the structural distortion, some tetrahedra appear in their surfaces and the inside spaces of the cages shrink, but about two interior atoms can still be inserted in for the clusters with 26–32 atoms. The sp^3 hybridization leads to a structural distortion which makes the number of dangling bonds decrease.

Acknowledgment

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