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Possible lowest-reactivity structure of the silicon cluster Si_{45}

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We propose a structure of the Si_{45} cluster through extensive search. This structure consists of two cages, where the outer cage contains threefold-, fourfold-, and fivefold-coordinated atoms. Our calculated local density of states of atoms in a concerned Si isomer shows that both threefold-coordinated Si atoms and fourfold-coordinated Si atoms with a back-bond are all active sites in the outer cage of this isomer. Especially, the number of the dangling-bond atoms in the outer cage of our lowest-energy isomer is significantly less than those of any previous structure for Si_{45} clusters. Therefore, our obtained lowest-energy structure of the Si_{45} cluster is a highly desirable candidate to serve as the lowest reactivity for the Si_{45} cluster.

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I. INTRODUCTION

Revealing the ground-state structures of larger midsized silicon clusters is a long-standing issue in the field of cluster physics. So far, much effort on the atomic structures of silicon clusters has been done in experiment. However, the experiments merely provided indirect structural information about the silicon clusters. For example, it is only inferred from the measured mobilities of Si clusters that the structures of Si_n are prolate for $n<24$ while oblate for $n>33$ and the both shaped structures (the prolate and oblate ones) coexist[1] in the range of 25–33. After examining the chemical reactivity of midsized Si clusters to some smaller molecules such as C_2H_2, NO_2, and so on, it was found that the chemical reactivity of Si_n (n=33, 39, and 45) is much lower than that of other sized Si clusters.[2] These observations probably correspond to the lower density of dangling bonds (DB's) in these Si clusters. Thus, scientists[3–5] have been stimulated to seek atomic structures containing a smaller amount of dangling bonds for Si_n (n=33, 39, and 45) clusters.

Early, Kaxiras[3] man-made a structural model of the Si_{45} cluster, in which the inner portion characterizes a tetrahedron structure. But there are about 40 dangling bonds existing in its surface. Such a large number of dangling bonds does not match the lower chemical reactivity of the Si_{45} cluster yet. Later on, with keeping the tetrahedron feature in the inner portion of each isomer, several groups[4,5] proposed different geometries for the Si_{45} cluster. Among them, a structural model without any dangling bond was generated by hand.[5] Unfortunately, our local-density-approximation (LDA) calculation[6] shows that this structural model of the Si_{45} cluster is very unstable. Alternatively, Andreoni, Rothlisberser, and Parrinello [7] proposed a double-shell isomer of Si_{45}, in which there are only seven dangling bonds existing at its outer cage. Such a small number of dangling bonds enables this structural model of Si_{45} to be the best candidate matching the lower reactivity of the Si_{45} cluster until now. It is worth noting that this structure was achieved through using the Car-Parrinello molecular dynamics, starting from a stuffed silicon fullerenelike structure.[7] Usually, it is fairly difficult to achieve the ground-state structure for an intermediate-sized silicon cluster at the level of first-principles molecule dynamics, owing to the heavy computational cost required. In this paper, combining a tight-binding (TB) approach and LDA calculations, we intensively search for the low-lying structures of Si_{45} clusters. An isomer of the Si_{45} cluster containing five dangling bonds is obtained, which is suggested to be more chemically stable than all previous candidates.

II. SEEKING PROMISING CANDIDATES

The tight-binding potential model for silicon used in this work was proposed with correction of the bonding environment around each Si-Si bond.[8] This potential model has been successful for seeking the promising isomers of midsized silicon clusters.[9] Owing to its high precision and simplicity, in this work we employ this TB potential model to search for promising candidates for the Si_{45} cluster.

It is noted that the Si_n clusters with $n>33$ most probably favor the stuffed fullerenelike structures energetically.[10] Thus, we select stuffed silicon-fullerene cages as starting structures. Initially, the possible ratios of the cage to the core are taken into account. All of the initial structures are relaxed with the treatment of the TB potential. We point out that, in the process of relaxation, the cage and core in a starting geometry are, respectively, fixed, followed by full relaxations. In addition, the relative orientation of the core to the outer cage is also adjusted randomly. The efforts above provide many different geometries of the silicon cluster we concerned with. Without a doubt, these structures are most probably metastable. If they are perturbed structurally, they will be probably transformed into more stable configurations. Motivated by this consideration, similar to Ref. 11, we perturb the low-energy structures obtained above by compressing them and then fully optimize the perturbed structures by using TB calculations. As a result, a lot of candidates of the Si_{45} cluster are provided. Through examining the structures of these candidates, we observe that all of the low-lying candidates feature the stuffed-fullerene structure still. Such an aspect is likely descended from the initial structures that have been the stuffed fullerene already. Therefore, it is possible that the obtained structures of these low-lying isomers are trapped into some local metastable states.

In order to avoid such a trap, we turn to other kind of starting geometries. Typically, a liquid silicon characterizes a random network, which is far distinct from the stuffed-fullerene structure as mentioned above. Thus we derive different portions from a liquid silicon randomly as another family of initial structures. With the iterative procedure of both compression and relaxation, we achieve a new group of metastable structures for the Si_{45} cluster at the level of the TB potential. Interestingly, we find that the low-lying isomers of silicon cluster Si_{45} obtained from the liquid silicon do exhibit fullerenelike structure. We emphasize that although the obtained promising candidates of Si_{45} by using the both methods are all stuffed fullerene, these stuffed-fullerene structures are not the same as each other. Here, the main discrepancy between these promising candidates is the different structures of the inner cores.

Overall, a lot of configurations of the Si_{45} cluster are considered unbiasedly. Based on the calculated energies of the resulting isomers of the cluster, we pick up about 200 isomers whose energies are within 1 eV above the lowest-energy isomer as promising candidates. Clearly, such a large amount of low-lying isomers cannot be efficiently handled by using any accurate LDA calculation, owing to the limitation of computational demands. Fortunately, the SIESTA code[12] offers a good compromise in both accuracy and computational demand between the TB potential method and accurate LDA calculations. So the selected candidates above are fully relaxed by using the SIESTA code with a double-ζ basis set and the generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange-correlation functional. From the relaxed structures of the considered isomers with the treatment of the SIESTA, we identify the top 20 candidates to serve as the inputs of calculations of the VASP (Vienna *ab initio* simulation package[13]) that is more accurate than the SIESTA. In the VASP calculations, the Perdew-Wang 91 exchange-correlation functional within generalized gradient approximation (GGA) is taken into account, and the value of the energy cutoff of 18 Ry is chosen for the plane-wave basis set. Finally, we obtain low-energy isomers of Si_{45} with the treatment of the VASP package. Figure 1 displays the top three structures of the Si_{45} cluster. The relative energies of the isomers of Si_{45}(a), Si_{45}(b), and Si_{45}(c) are 0.0, 0.78, and 1.09 eV, respectively. Strikingly, these isomers characterize 9@36, being consistent with the previous result.[7] Another aspect in the promising candidates we proposed is that the inner core in each isomer exhibits cagelike structure as displayed in Figs. 1(d)–1(f). Thus, our predicted lowest-energy structure of the Si_{45} cluster exhibits two cages. We emphasize that this two-cage structure is far distinct from any reported structures for the Si_{45} cluster.

On the other hand, our calculations show that the lowest-energy isomer obtained from the VASP calculation is also the minimal-energy structure obtained at the level of either the SIESTA calculation or the TB calculation we used. This again demonstrates that the TB potential we used here is an excellent tool to search for promising candidates of Si clusters.

III. CHEMICAL REACTIVITY AND DISCUSSION

As we know, a cluster reacting with an adsorbate is mainly attributed to the reaction of the adsorbate with some active atom(s) in the outer surface of the cluster. Thus, we pay attention to the active sites in the outer shell of each Si_{45} isomer obtained above. Structurally, there are threefold-, fourfold-, and fivefold-coordinated atoms existing at the outer cage of each low-lying isomer cluster. Among these Si atoms, the threefold-coordinated Si atom having one dangling bond is very active in a Si cluster, whereas the fivefold-coordinated Si atoms in a Si cluster are almost inactive owing to no unpaired electron being left in these atoms. As for the fourfold-coordinated Si atoms in the outer cage of a Si cluster, they are classified into two groups in terms of the local atomic geometry around each fourfold-coordinated Si: The fourfold-coordinated Si atom plus its first neighboring Si atoms form a tetrahedronlike or pyramidlike configuration. Especially, in the case of the pyramidlike configuration, the fourfold-coordinated atom has a backbond that connects this fourfold-coordinated Si atom in the outer cage with a Si atom in the inner core. For convenience, this kind of fourfold-coordinated Si atom is named BB-4 atom. Usually, the back-bonds described above are weak so that the BB-4 atoms do not stabilize the structure of the cluster very well. In the meantime, unlike a fourfold-coordinated Si atom featuring a local tetrahedron structure, the BB-4 atoms are chemically active to some extent. Thus, both threefold-coordinated Si atoms and BB-4 atoms in the outer cage of a Si_{45} isomer contribute to the reactivity of this Si cluster.

We point out that the analysis above is made according to the relation between the bonding character and the local structural configuration around each typical Si atom in a Si_{45} cluster. In the view of electronic structures, a cluster reacting with an adsorbate means that the frontier molecular orbitals of the cluster overlap with the related frontier orbitals of the adsorbate effectively. For a cluster, the energy levels corresponding to the frontier orbitals are close to the Fermi energy level. The larger the number of energy levels close to the Fermi level of a cluster is, the more active the cluster is. On the other hand, if some of the eigenstates corresponding to the energy near the Fermi level are dominantly contributed from one or several typical atoms in the cluster, these atoms are the active sites. So the relative reactivity of Si atoms with different coordinations in a Si cluster can be reflected in the local density of states (LDOS) near the Fermi energy level. As a representative example, Fig. 2 displays the calculated LDOS per atom for the DB and BB-4 as well as fivefold-coordinated atoms in the outer cage. The LDOS per atom for the Si atoms in the core and the total density of states per atom for the entire Si_{45}(a) are also plotted in Fig. 2. Obviously, within 1.0 eV below the Fermi energy level, the LDOS arising from a DB atom are the largest and from a fivefold-coordinated Si atom are the smallest, whereas the LDOS arising from a fourfold-coordinated Si atom with one back-bond are just between these two extreme cases in the considered energy range. These features in the calculated LDOS of the different kinds of Si atoms demonstrate that both the three-coordinated Si atoms and the fourfold-coordinated ones with a back-bond in the outer cage of a Si cluster are

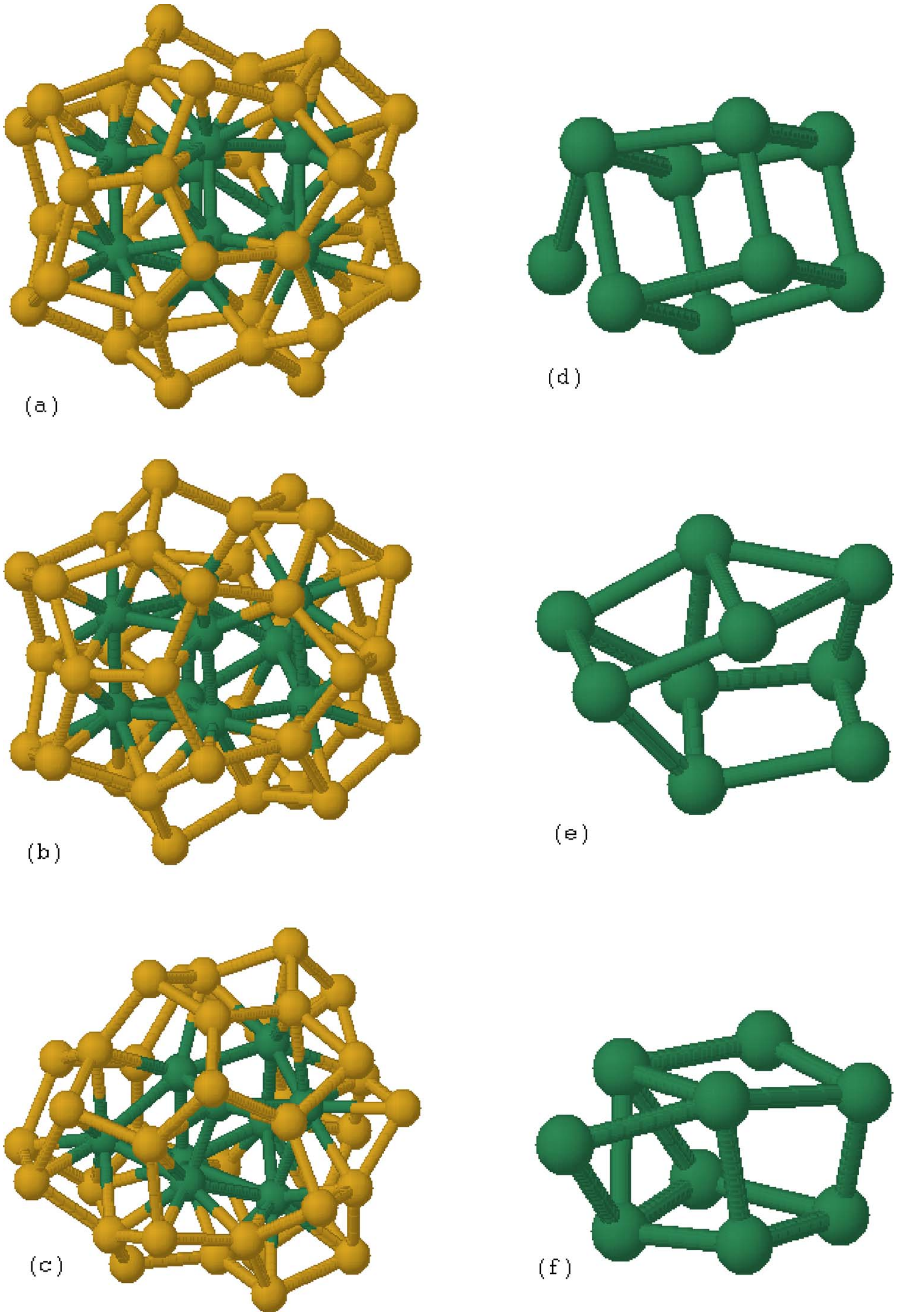

FIG. 1. (Color online) Three low-lying structures of the Si_{45} cluster. The inner portions in (a), (b), and (c) are, respectively, shown in (d), (e), and (f).

indeed chemically active. Because of this, the density of active sites consisting of the dangling bond atoms and the BB-4 atoms in the outer surface of a Si_{45} isomer is a critical factor to understand the reactivity of the isomer. We therefore count the number of dangling bond atoms and BB-4 atoms for the proposed low-lying isomers of the Si_{45} cluster. With using a cutoff value of 2.75 Å, which is the same as that used in Ref. 7, we obtain the number of DB's and the number of BB-4 atoms as well as the densities of these active atoms in the low-lying isomers of the Si_{45} cluster, as summarized in Table I.

From Table I, we find that the number of dangling bonds in the low-lying isomers of Si_{45}(a), Si_{45}(b), and Si_{45}(c) are 5, 6, and 4, respectively, being significantly smaller than those reported previously.[3–5,7] As mentioned before, the previous work assessed the relative reactivity of different isomers of the Si_{45} cluster through comparison of the density of DB's between different isomers only. When following such an assessment, the chemical reactivity of our proposed isomers of Si_{45} shown in Fig. 1 are all less than that of any previous candidate. On the other hand, among the proposed isomers of Si_{45}(a), Si_{45}(b), and Si_{45}(c), the number of DB's in the third isomer is the smallest than the others, even though this isomer is not the most stable. However, when the BB-4 atoms are taken into account, the density of total active sites in the lowest-energy isomer $[Si_{45}(a)]$ is lower than the others.

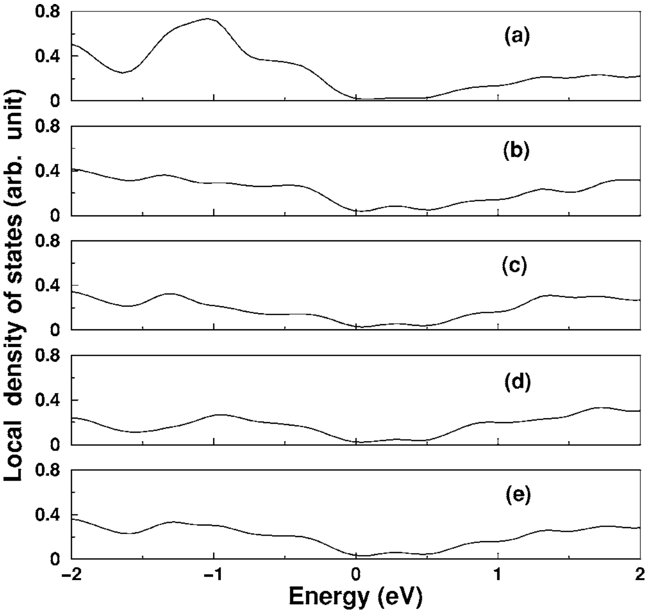

FIG. 2. The calculated local density of states of (a) a dangling bond Si atom, (b) a fourfold-coordinated Si atom with one back-bond, (c) a fivefold-coordinated Si atom, (d) a Si atom in the core, and (e) the total density of states per atom in the whole cluster Si_{45}(a).

Moreover, the order of the relative energetic stability of the three isomers of the Si_{45} cluster is just the same as that of the relative chemical reactivity of these isomers.

It is worth noting that experiments have already revealed that the Si_{45} cluster is the most chemically stable in comparison with its neighboring clusters. Hence, it is necessary to qualitatively compare the chemical reactivity of our isomers of Si_{45} to the neighboring clusters Si_{44} and Si_{46} at least. For this purpose, similar to the process of seeking the promising candidates of Si_{45} cluster above, we extensively search the low-lying isomers for both Si_{44} and Si_{46} clusters. The obtained low-lying isomers of Si_{44} and Si_{46} clusters (Fig. 3) exhibit fullerenelike structures too, with inclusions of eight Si atoms inside their cages. After examining the atomic structures of these isomers, we find that the densities of active sites in the outer cages of the two clusters are all larger than that of $\mathrm{Si}_{45}(a)$. Thus, the chemical reactivity of the achieved lowest-energy isomer of the Si_{45} cluster is lower than that of its nearest neighbors, in qualitative agreement with the observation from experiments.

TABLE I. The number of DB's (N_{DB}), fourfold-coordinated Si atoms with a back-bond ($N_{BB\text{-}4}$), fivefold-coordinated Si atoms (N_5), and the density of active sites, ρ, in the outer cage of each considered isomer. Here, $\rho=(N_{DB}+N_{BB})/N_{cluster}$, where $N_{cluster}$ is the number of total atoms in a cluster.

	N_{DB}	$N_{BB\text{-}4}$	ρ (%)	N_5
$\mathrm{Si}_{45}(a)$	5	14	42	17
$\mathrm{Si}_{45}(b)$	6	16	49	14
$\mathrm{Si}_{45}(c)$	4	20	53	12
Si_{44}	6	20	59	11
Si_{46}	6	15	46	7

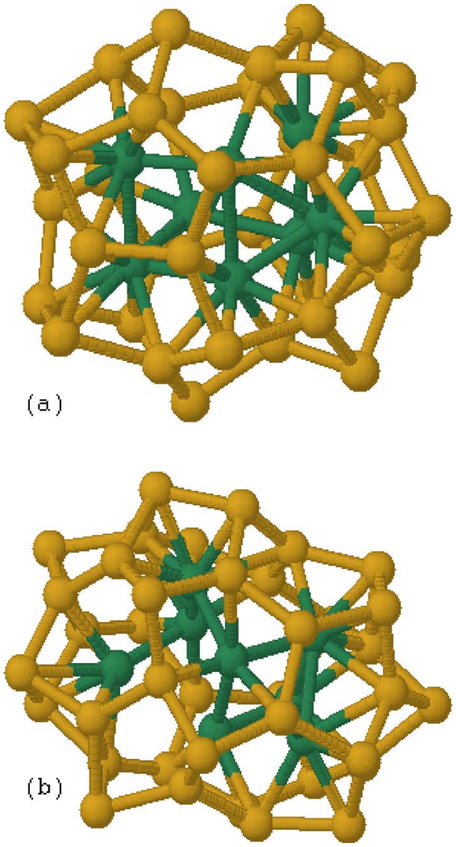

FIG. 3. (Color online) Low-lying structures of (a) Si_{44} and (b) Si_{46}.

We emphasize that the low density of active sites in the proposed isomers of Si_{45} is not only associated with the low reactivity of the isomers, but regarded as an important factor corresponding to the energetic stabilities of these isomers as well. Structurally, it is observed that the dangling bonds in each concerned isomer are not adjacent, which are analogous to the rest atoms in a Si(111)(7×7) surface;[14] the fourfold-coordinated Si atoms with a back-bond in the outer cage of an isomer are somewhat analogous to the adatoms in a Si(111)(7×7) surface.[14] In addition, there are five, four, and two Si dimers that are off the outer cages of Si_{45}(a), Si_{45}(b), and Si_{45}(c), respectively. These Si dimers are quite like the dimers in the dimer walls of a Si(111)(7×7) surface. Correlating the number of the Si dimers as mentioned above to the stability of the related isomer, we may propose that the Si dimers at the Si cage in the Si_{45} cluster are probably another significant factor to stabilize the isomer. In fact, each of these Si dimers can be regarded as the rebonding between two neighboring dangling bonds to form a local π bond at the outer cage, lowering the energy and reducing the chemical reactivity of the isomer.

All efforts above mainly focus on seeking low-lying isomers of the Si_{45} cluster and analyzing the reactivities and stabilities of the proposed low-energy isomers. Without a doubt, providing more information about the proposed low-lying isomers is of importance. For this purpose, we calculate the values of the ionization potential (IP) and electron affinity (EA) for the three low-lying isomers of the Si_{45} cluster using the SIESTA package, in which the generalized gradient approximation at the level of Becke-Lee-Yang-Parr (BLYP) and double-ζ plus a polarization basis set are taken into account. Our calculated IP's of Si_{45}(a), Si_{45}(b), and Si_{45}(c) isomers are 5.5, 5.3, and 6.2 eV, respectively, and the EA's of these isomers are 2.18, 2.12, and 2.12 eV, respectively. Strikingly, the calculated IP value of Si_{45}(a) matches the experimental value (5.5–5.6 eV) very well.[15] Such a good agreement strongly supports the conjecture that the proposed lowest-energy isomer Si_{45}(a) is probably a leading candidate for the Si_{45} cluster.

IV. SUMMARY

In conclusion, based on our extensive search, we obtain a lowest-energy isomer of Si_{45}, which consists of two cages. The outer cage in this structure is modulated by the dangling-bond atoms, fourfold-coordinated atoms, and fivefold-coordinated atoms. Our analysis shows that both the dangling-bond atoms and fourfold-coordinated atoms with a back-bond are all the active sites in the outer cage of the isomer. Importantly, we find that the number of dangling bonds in this isomer is significantly lower than all previous structures of the Si_{45} cluster. Therefore, the predicted structure of Si_{45}(a) in this work is probably a leading candidate associated with the lowest reactivity for the Si_{45} cluster.

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