Structure of Nanoscale Silicon Clusters

Ursula Röthlisberger,* Wanda Andreoni, and Michele Parrinello
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

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Using the Car-Parrinello method, we have obtained unforeseen structures for the low-lying isomers of Si_{45} and other midsized Si clusters. They are formed by two shells of atoms, the outer one (cage) being fullerenelike and the inner one (core) consisting of a few atoms saturating dangling bonds. These novel structures provide for the first time a consistent interpretation of the available experimental data, including the reactivity trends and the structural transition at a size of ~ 25 atoms.

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The drive towards nanoscale technology has motivated intensive research [1] on small Si_n clusters. They are a new form of Si with properties different from those of bulk phases. Information on their properties is often obtained in an indirect manner, for which we have to rely on sophisticated experiments. The structural properties of clusters with $n \leq 10$ are relatively well understood through a combination of experiments [2] and theory [3,4]. The structure of the larger clusters is still a puzzle, but the following experimental facts are known. (i) The abundance spectrum exhibits neither special features nor magic numbers [5]; (ii) the shape changes from prolate to "more spherical" in the narrow range between $n \simeq 24$ and $n \simeq 30$ [6]; (iii) the dissociation energy, which is strongly size dependent in the smaller clusters, becomes a smooth function of n and exhibits no magic numbers for $n \gtrsim 25$ [7]; (iv) the reactivity to several molecules [5,6(b),8–10] is lower by 2–3 orders of magnitude than that of the most stable Si surface, namely, the (7×7) Si(111) surface; and (v) it exhibits minima at $n=33$, 39, 45 [5,8(c),9] for well-annealed clusters.

To date, theoretical work has been focused mostly on Si_{45}. Several models have been proposed that have some features in common, i.e., one central atom tetrahedrally coordinated as in bulk Si, and a high degree of symmetry which implies a nonprolate shape, in agreement with (ii). The structures proposed by Kaxiras [11] (I) and by Pattersson and Messmer [12] (II) have a large number of dangling bonds (DBs) (40 and 28, respectively), which is at odds with reactivity data. In contrast, the structure proposed by Jelski *et al.* [13] (III) has no DBs, but contains several features that are energetically costly for Si, i.e., sixfold-coordinated caps, short bonds, and triangular and tetragonal facets.

Such a situation calls for a less biased approach to the structural issue combined with the accuracy of an *ab initio* treatment of the interatomic interactions. We have applied the local density approximation based Car-Parrinello method [14], which has been demonstrated to provide an accurate description of Si properties in a large variety of chemical situations [4,15]. An extensive set of calculations leads us to propose here a novel picture for midsized Si clusters. The transition from a prolate to a more spherical shape reflects a dramatic change in structure. For $n \lesssim 20$ the atoms are arranged on one shell and form triangular surface facets [16]. For $n \gtrsim 20$ a totally new class of structures occurs. The atoms are organized into two shells. The outer one has the topology of a fullerene [17] cage [18]. The atoms in the inner shell have a high coordination number and saturate most of the DBs of the outer shell. The saturation is optimal in a relative sense at $n=33$, 39, 45, leading to the observed reactivity minima.

Most of our calculations have been performed on Si_{45}. The technical details are identical to those in Ref. [4]. We treat the core electrons in the nonlocal pseudopotential approximation and expand the Kohn-Sham orbitals in plane waves [19]. We have tested the stability of the previously proposed structures (I–III) [11–13] and found that all of them rearrange easily to substantially reconstructed geometries of lower symmetry. Interestingly, mere relaxation already leads both structures (I) and (II) to new locally stable configurations with a drastically reduced number of DBs. Distortion of the tetragonal facets and broadening of the bond length distribution characterizes instead the first steps of the spontaneous reconstruction of model structure (III).

As a result of a complex search strategy, we have been able to generate structures that are much lower in energy (at least by ~ 6 eV) than all previous models I–III. We first performed two very lengthy simulated annealing runs that started with different initial conditions: one from structure I, which has a buckled fullerenelike cage of 44 atoms with one tetrahedrally coordinated atom at the center [20], and the other from a highly coordinated dodecahedral structure. The latter is rather unlikely for a Si cluster, but is easily disrupted and provides an unbiased starting point. In such a complex system, the probability that the system will attain its global minimum in a finite-time-scale annealing run is vanishingly small. Nonetheless, the results of careful annealing can produce valuable indications of the main features of the optimal structures. In spite of the different initial conditions, the two runs led to very similar structures of comparable energies (lower than the models discussed above by at least ~ 4 eV). The atoms were arranged approximately into two shells: an inner shell containing a few core atoms and an outer one forming a distorted cage consisting al-

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most exclusively of fivefold and sixfold rings and thus clearly reminiscent of a fullerene topology [17].

Starting with these configurations, we applied a more complex optimization strategy. Imposing symmetry constraints and/or removing what appeared to be local defects provided a first "sample purification," which was followed by extensive relaxation free of symmetry constraints. This iterative procedure led to a manifold of isomers, among which the lowest energy configurations were ~ 2 eV lower than the direct results of the annealing. All of them were characterized by a clear two-shell topology (the average radii of which differed by ~ 4 a.u.) and the outer shell had a perfect fullerenelike [18] network of 38 atoms. Unlike carbon fullerenes, however, these cages were buckled as a consequence of the much higher tendency of Si to form distorted sp^3 hybrids. This also makes the two shells strongly interconnected, in contrast to the onionlike structures observed for large carbon aggregates [21]. All the cage atoms form three short bonds on the cage itself and most of them form additional (one or two) bonds with the internal atoms. The role of the core atoms emerges clearly; namely, they stabilize the outer cage by reducing the number of DBs. This is reminiscent of some of the reconstructions observed in semiconductor surfaces where adatoms stabilize the surface by saturating DBs [22]. Here the surface is the fullerenelike [17] cage but the adatoms are placed inside, forming an inner shell. At variance with the adatoms on surfaces, the core atoms interact strongly with each other due to their close proximity.

The structural analysis of our limited set of isomers also revealed that the stabilization of the Si fullerenelike cage can be achieved in many ways by varying its buckling and the arrangement of the internal atoms. In fact,

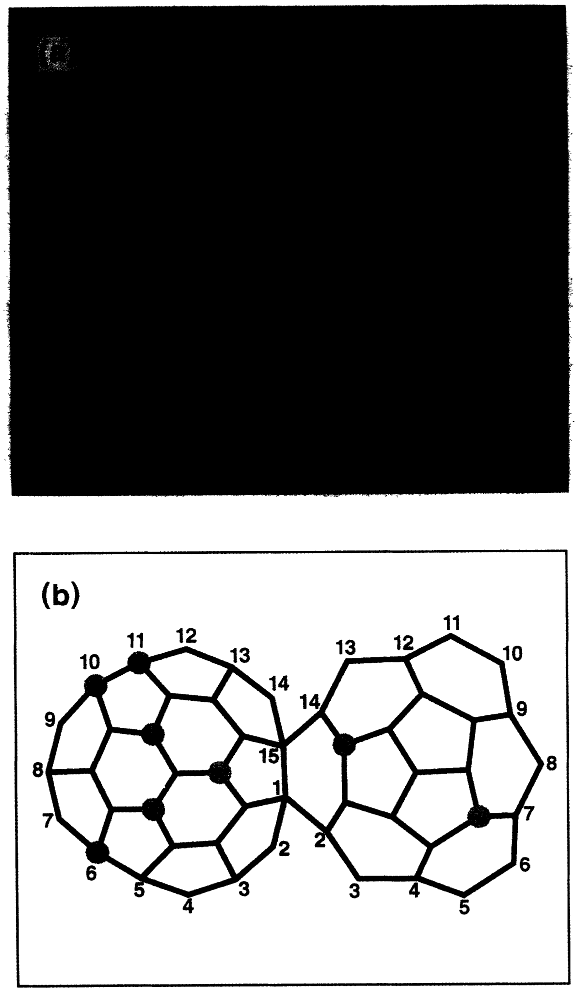

FIG. 1. Si_{45}: a 38+7 isomer: (a) structure, with distinct cage (yellow) and internal (red) atoms; (b) bidimensional view of the cage, with circles denoting the DBs (defined within a cutoff of 5.2 a.u.). The cut is along the bonds; numbers denote identical atoms of the upper and lower halves.

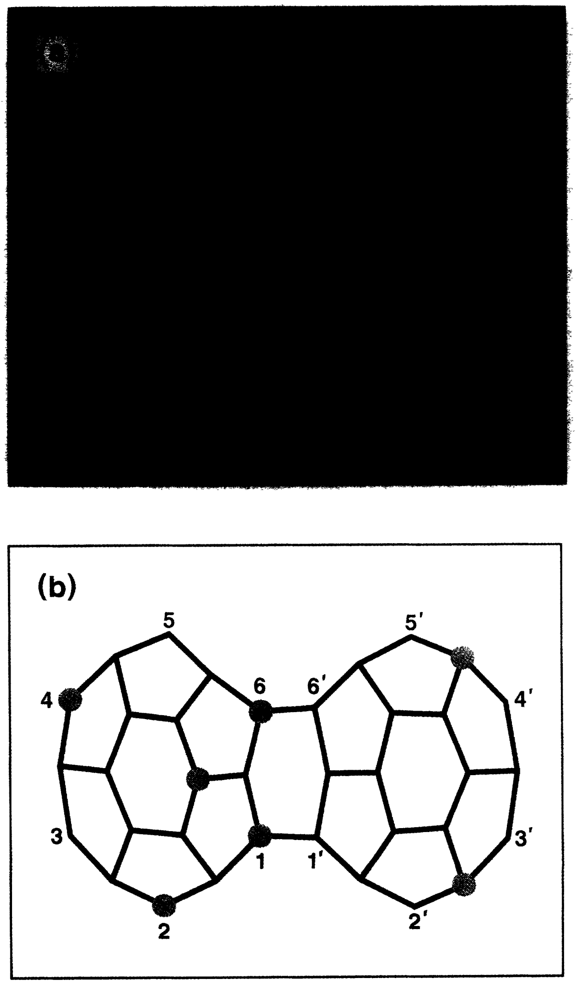

FIG. 2. Same as Fig. 1 for a 36+9 isomer. In (b) the cut is through the bond centers in the equatorial region; numbers denote the atoms that form bonds between the upper and the lower halves (i.e., 1 → 1′, 2 → 2′, etc.).

for the lowest energy configurations of the 38-atom cage structures, we find as many as six distinct isomers that are degenerate within 0.1 eV. Figure 1 shows (a) a representative example and (b) the distribution of the DBs.

The result of the iterative annealing process suggested that other fullerenelike cages with encapsulated atoms could provide further relevant isomers for Si_{45}. A 36-atom cage was the natural alternative candidate. Two initial cage configurations were considered, one of which ended up as an isomer degenerate with the lowest 38-atom cage isomers and the other was lower by only ~ 0.4 eV. This structure is illustrated in Fig. 2(a). Two competing factors lead to the closeness in energy of the two families of clusters. The 36-atom cage has a reduced number of DBs [see Fig. 2(b)] (1 or 2 less) but has a higher mechanical stress and on average a higher coordination between the core atoms (2.6–3.2 instead of 1.4). In either case, these are globally highly coordinated (average coordination ~ 7). Given the tendency of bulk Si to increase coordination under pressure, this finding may not be surprising with regard to the encaged atoms. They not only act as internal caps that saturate the surface but are also linked with each other. Different geometries are possible. They range from sixfold rings in chair conformation, reminiscent of diamond, to more compact arrangements similar to those of the small bare clusters [3,4]. Clearly, the key characteristics of the structures obtained here for Si_{45}, namely, the presence of the sp^3-like configuration for the outer shell atoms and of a highly coordinated core, contrast with those of the three previously proposed models.

The symmetry of all low-energy isomers is at most C_s. Although the fullerene cages might have a higher degree of symmetry [23], the sp^3-hybridization-driven buckling as well as the presence of the encapsulated atoms lead to a lowering of symmetry. Imposing explicitly symmetry constraints leads invariably to unstable structures. In spite of their low symmetry, the energetically favorable structures reveal only slight deviations from sphericity. We did not consider cages with a number of atoms less than 36 or more than 38. The excessive confinement of the core atoms strongly disfavors a smaller cage, as we have checked by introducing an additional atom inside the 36-atom cage. Instead, by augmenting the core of a $38+7$ cluster, we obtained a stable Si_{46} isomer, at no expense in either cohesive energy or number of DBs. Too few core atoms, on the other hand, make the saturation of the DBs inefficient and larger cages unlikely. We have tested this point by removing one core atom from the $38+7$ cluster. After free relaxation, the fullerenelike cage was preserved but the number of DBs increased by 5 and the cohesive energy decreased by 0.06 eV/atom. We have also explored the stability of a Si_{33} cluster built from a fullerenelike outer shell of 28 atoms. Relaxation proved that this type of configuration is highly stable. The atom-centered structure proposed by Kaxiras [11] for Si_{33} with five fourfold-coordinated internal atoms was unstable. Instead, in the stable configuration the atoms of the internal cluster (a distorted trigonal bipyramid, resembling Si_5^3) have an average global coordination of ~ 8, the number of DBs is 4, and the cohesive energy is only 0.04 eV lower than that of Si_{45}.

The above results suggest the following picture. All the Si clusters in the size range corresponding to diameters of the order of 1 nm are endohedrally "self-doped" "fullerenes" [18]. These structures are substantially different from the so-called "filled fullerenes" (Ref. [8(c)]), i.e., fullerenes with one central and tetrahedrally coordinated atom and (in some cases) external capping atoms. We find these geometries to be unstable, as discussed for Si_{45} (model I) and Si_{33}. Our calculations show that the nanoscale clusters constitute a form of aggregation clearly distinct from the lower size regime. They are rather spherical in contrast to the Si_n clusters with $10 \leq n \leq 20$, which assume predominantly prolate shapes [16], in agreement with experiments (ii) [6]. This transformation does not significantly alter the average atomic coordination in the cluster, however, in agreement with the absence of a systematic change in reactivity to C_2H_4 in the region of the transition [6(b)].

The picture of the silicon cluster chemistry that emerges from our calculations is consistent with what is already known for surfaces and bulk phases, i.e., a pronounced tendency to fourfold coordination. This is in obvious contrast to the structural models proposed by Kaxiras [11] and more recently by Kaxiras and Jackson [24], where the predominant coordination of the silicon atoms is three, both below and above the shape transition. Their assumption appears rather unlikely and in light of the present calculations is unnecessary to explain the shape transition.

Several families of isomers exist and can be classified according to the number of atoms in the cage. There are at least four such families: Si_{28+n_c}, Si_{32+n_c}, Si_{36+n_c}, and Si_{38+n_c}. For each of them a maximum possible value of n_c exists that leads to an optimal saturation of DBs and to clusters of relatively low reactivity (v) [8], e.g., Si_{33} ($n_c=5$), Si_{39} ($n_c=7$), and Si_{45} ($n_c=9$). In each family, several distinct isomers are possible, depending on the topology of the fullerenelike cage [17,23], the type of buckling, and the structure of the core. While isomerization within the same family is fast, interconversion within different families is expected to have relatively high activation barriers. In agreement with experiments [(i), (iii)], the calculated binding energies (Si_{33}, Si_{44}, Si_{45}, Si_{46}) show no particularly stable "magic" cluster. In addition, the gaps between the highest occupied and the lowest unoccupied molecular orbitals are all of the order of a few tenths of an electron volt. This points to the lack of correlation between thermodynamic stability and chemical reactivity in these clusters, in agreement with Ref. [9].

Besides the number of DBs, other factors also contribute to chemical reactivity, i.e., dynamic, kinetic, as well as steric effects. Of the latter, the spatial distribution of the DBs is relevant. We find no adjacent DBs for the Si_{33} structure or for the 36+9 isomers of Si_{45} [Fig. 2(b)], and at most one pair for the 38+7 isomers [Fig. 1(b)]. A low density of DBs for the midsized Si clusters is consistent with several observations and in particular with the fact that they are less reactive than Si surfaces (iv). Also, when the clusters are exposed to NH_3, they exhibit a characteristic behavior, i.e., only very few molecules are adsorbed at low temperature and dissociative chemisorption occurs only at $T \gtrsim 470$ K. With increasing temperature the density of DBs increases due to the bond lengthening, and leads to dissociative chemisorption [8(b)]. Our simulations of the 38+7 clusters at ~550 K support this picture.

In conclusion, our calculations reveal a novel structural pattern for the nanoscale Si clusters and establish a further link between the chemistry of silicon and that of carbon. They also provide a sound basis for the understanding of the available experimental data. In order to further confirm this picture, more experimental data, such as vibrational and electronic excitation spectra, are highly desirable.

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*Present address: University of Philadelphia, Department of Chemistry, Philadelphia, PA 19104-6323.

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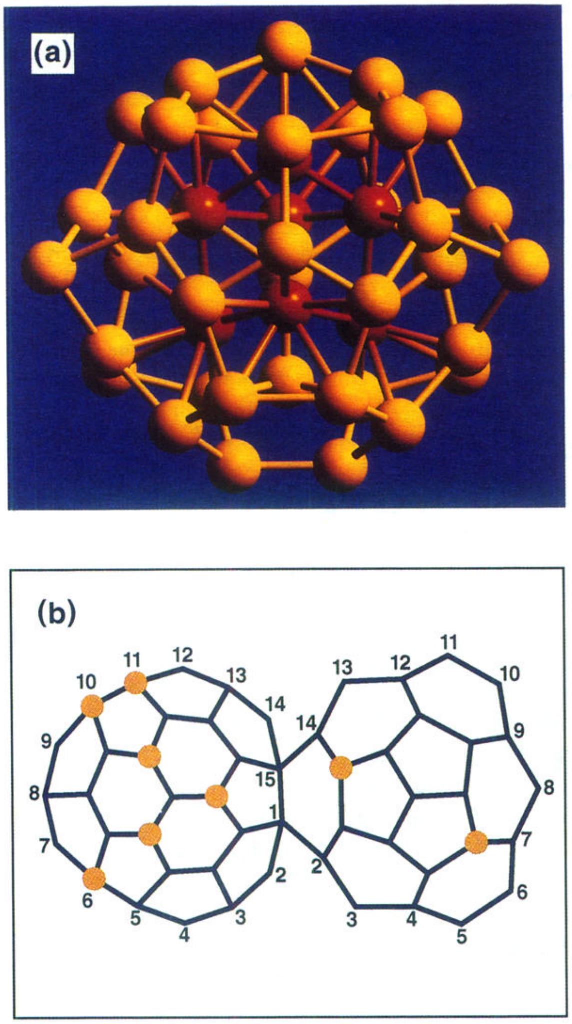

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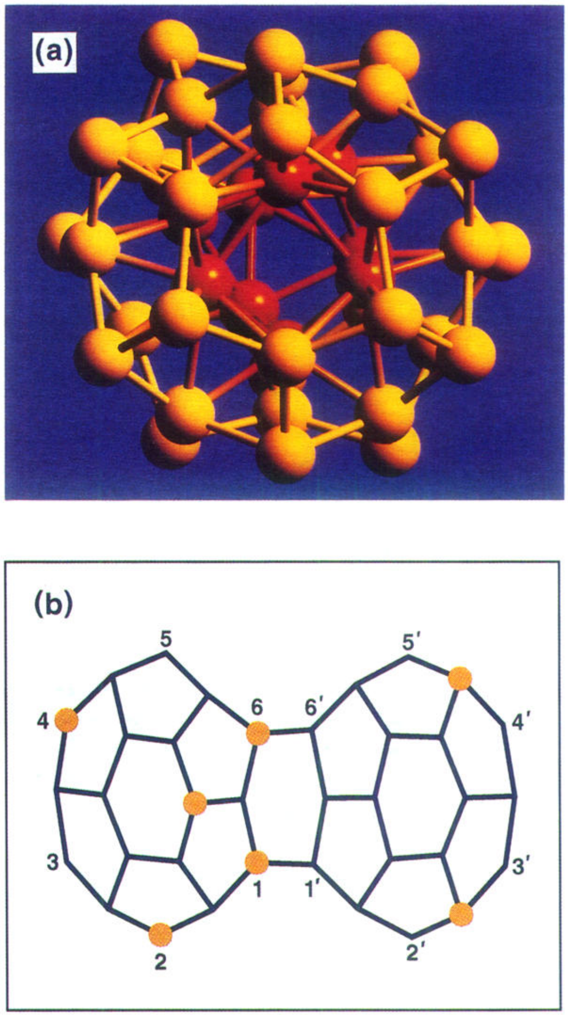

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