Shape of Small Silicon Clusters

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We propose an explanation for the experimentally observed transition in the shape of silicon clusters of size $20 \leq N \leq 40$: Elongated shapes of low energy can be obtained by stacking stable subunits, while concurrent optimization of surface-to-volume ratio and surface structure leads to compact shapes. A transition in shape from elongated to compact structures is expected as the size increases beyond a critical value at which interior atoms become stable. Our proposal is backed by extensive first-principles calculations on the energetics of two classes of Si clusters, which suggest a critical size bounded by $24 \leq N \leq 28$, in good agreement with experimental observations.

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The study of small clusters of atoms has been producing unexpected results for the last several years. One of the recent surprises was the observation by Jarrold and co-workers [1,2] that the *shape* of small Si clusters, containing N =20–40 atoms, depends on their size. Specifically, it appears that clusters of prolate shape are prevalent for sizes up to 27, whereas for larger sizes a more spherical oblate shape dominates. This striking observation brings a new dimension to a much debated question: What exactly is the structure of nanoscale Si particles and how does it evolve to that of the macroscopic crystal as the size increases? [3] Up to now, mostly spherical and compact clusters have been considered as theoretical models attempting to address this question (the only exception being Phillips' qualitative arguments for elongated models, see Ref. [4]). Indeed, in a small cluster, where most of the atoms are on the surface, one might expect the shape that minimizes the surface area to dominate. Thus, if a cluster were able to change its shape without large energy cost it would tend to be spherical. An apt analogy is the liquid-drop model invoked to describe the shape of atomic nuclei [5]. The new aspect that Jarrold's experiments introduce to the debate is that the overall shape, as well as the local structure, can depend on the size of the cluster. The apparent strong dependence of structure and shape on the size of these microscopic particles cannot be addressed by classical macroscopic theories such as, e.g., Landau's derivation of crystal shape from surface-tension anisotropy [6]. The present work attempts to address this issue by examining cluster stability as a function of size and shape using first-principles quantum mechanical total-energy calculations on a range of representative models of silicon clusters.

As has been pointed out in the literature [7], it is a mathematically intractable task to find the optimal structure of a cluster in the size range of interest ($N \geq 20$), even if one were to use a simple classical potential to model atom-atom interactions. For instance, a recent exhaustive study for ground-state structures of Si clusters using first-principles molecular dynamics has addressed sizes only up to *five atoms* [8]. In fact, since several energetically comparable isomers are likely to exist at large sizes, finding the optimal structure for a given size is not the desirable approach. For these reasons we have chosen a different approach, that is, we study in detail two distinct types of structures. The first type consists of puckered sixfold rings of atoms, stacked along a central axis of threefold rotational symmetry and capped by single atoms at either end. This stacking produces elongated (i.e., prolate) structures. The second type features a more compact geometry, with as many interior atoms and a shape as nearly spherical as possible. Both structure types were motivated by analogy to bonding in the bulk and on Si surfaces. In particular, the puckered sixfold rings in the elongated clusters are borrowed directly from the diamond lattice, whereas the arrangement of the surface atoms in the compact class resembles that of Si surface reconstructions. The similarity to surface reconstructions has been proposed to explain relative stability and possibly sharp variations in chemical reactivity for clusters in a somewhat larger size range (30–50 atoms) [9].

The two classes of structures we consider here may not actually contain the energetically most favorable geometries. Their merit is that they represent two qualitatively different ways of producing successively larger clusters with the same type of chemical bonding (predominantly covalent, as in bulk Si). Clusters of elongated shape might exist if a particular unit of atoms shows exceptional stability, so that a stacking of such units becomes a favored mode of growth. On the other hand, if minimization of surface area were a dominant consideration, a spherical cluster shape would obtain, provided that favorable bonding arrangements are consistent with this shape. The competition between the two trends is precisely what our two classes of models attempt to capture.

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In the first class a stable unit of covalently bonded atoms is repeatedly stacked along one axis, giving elongated shapes without changing bonding and coordination. In the second class the most compact structure is sought for a given cluster size, consistent with predominantly covalent bonding. This produces significant changes in coordination as the cluster size increases. Thus, the comparison of these two classes can reveal the importance of *shape* as a function of size, while other factors, such as the nature of bonding, are kept fixed. We have also considered variants of the two classes, and find that they follow the same trends.

We have performed first-principles total-energy calculations for clusters of both types over the size range $N =$ 20 to 33 atoms. This range brackets the size at which experiments show the intriguing transition in cluster shape [2]. The calculations described here are based on density functional theory, in the local density approximation (LDA) [10], a quantum mechanical theory that predicts bond lengths and bond angles in molecules and solids to within a few percent of experiment [8]. We also include the recently developed generalized gradient approximation (GGA) for the exchange and correlation energy functional [11], which has been shown to give a marked improvement over LDA in the binding energy of finite systems [12]. We use a basis of Gaussian orbitals and a numerical integration scheme [13] with a mesh that can be systematically refined to deliver very high accuracy in the energies. Optimized geometries for each structure are obtained by conjugate gradient minimization of the calculated Hellmann-Feynman-Pulay forces on the atoms [13]. The atom positions are relaxed until the average force on an atom becomes less than 0.01 a.u. (further relaxation of the structure was found to have a negligible effect on the binding energy). The binding energy per atom E_B for the relaxed cluster is then obtained from the GGA, with the energy of a free Si atom as a reference.

We discuss first the structural features of our models. The puckered sixfold rings of the elongated structures are similar to the rings along the $\{111\}$ crystallographic direction in bulk Si. The rings are stacked along a central axis and are capped by single atoms at either end. These structures have oblong shape, with the central axis longer than the ring diameter. Every atom is on the cluster surface and has threefold coordination. Ring structures were studied for the $N = 20$, 26, and 32 atom clusters. The 20- and 26-atom ring structures are shown for illustration in Figs. 1(a) and 1(b). One variant of this structure is a 28-atom cluster, which contains two atoms in the center, joining two 13-atom sections composed of two rings and one cap each. This is shown in Fig. 1(c). The two central atoms are fourfold coordinated.

The compact structures have shapes closer to spherical. Except for the 20-atom cluster [a perfect dodecahedron shown in Fig. 2(a)] and the 26-atom cluster [Fig. 2(b)], the compact clusters include interior atoms with at least fourfold coordination, while the surface atoms have at least threefold coordination. The 26-atom compact cluster consists of two hemispherical domes of ten atoms joined by a ring of three dimers. The dimers have a structure that closely resembles the dimer bonds on the Si(100)-(2 × 1) surface reconstruction. The 10-atom

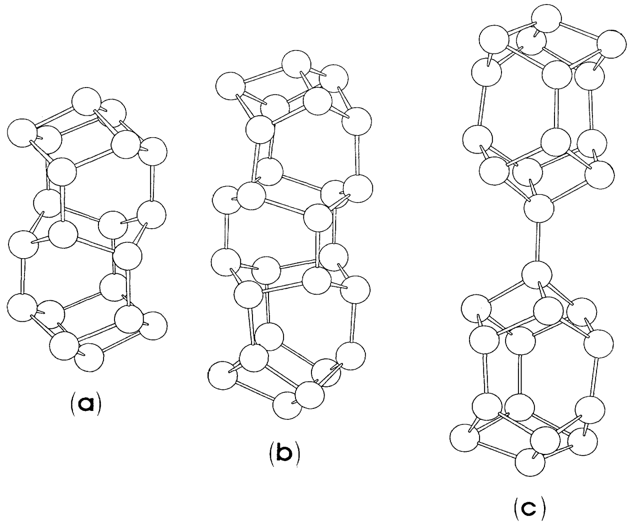

FIG. 1. Representative elongated structures formed by stacking puckered sixfold rings with two single-atom caps at either end. (a) 20-atom structure; (b) 26-atom structure; (c) 28-atom structure, obtained from the 26-atom structure by addition of two atoms in the center.

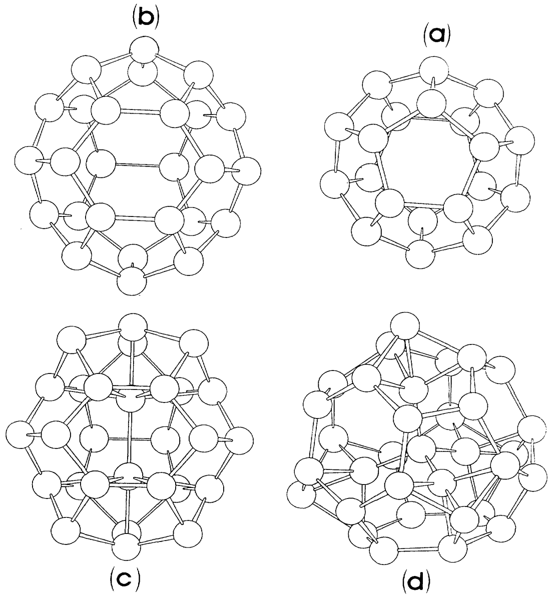

FIG. 2. Representative compact structures. (a) The 20-atom dodecahedron; (b) the 26-atom structure formed by two 10-atom domes joined through three dimer pairs; (c) the 28-atom structure formed by addition of two interior atoms to the 26-atom structure; (d) the 33-atom structure with T_d symmetry, resembling the surface reconstruction of Si(111)-(7 × 7).

domes can be continuously deformed without any bond breaking to obtain the tetra-capped octahedron, one of the lowest-energy geometries for size 10 [14]. The 28-atom cluster has the same structure as the 26-atom cluster, with the addition of two interior atoms [Fig. 2(c)]. An alternative model for a 28-atom cluster is inspired by the fullerene structure [15], and consists of pentagonal and hexagonal rings on a cage with empty interior. The 33-atom cluster [Fig. 2(d)] has perfect tetrahedral (T_d) symmetry, it contains five interior atoms with fourfold coordination and has a surface reconstruction which is locally similar to the 7×7 reconstruction of the Si(111) surface (for details see Ref. [9]). The 29-atom structure is a derivative of the 33-atom structure, with the four outermost atoms [which correspond to the "adatoms" of the Si(111)-(7×7) reconstruction] removed. This cluster retains the T_d symmetry of the 33-atom cluster. Finally, we have considered a compact but nonspherical structure of 27 atoms arranged in a simple cubic geometry (O_h symmetry). This structure has a single sixfold coordinated atom in the center, but is not a perfect cube, due to significant relaxation of the surface atoms.

The binding energy per atom for the various clusters studied is shown in Fig. 3. The results strongly suggest that there is a transition in the shape of the most stable clusters as their size increases: The smaller clusters prefer the elongated shape, while for the larger clusters, the compact structures are more favorable. The existence of this transition can be understood, in general terms, by a surface-to-volume argument: For spherical clusters of size N the binding energy per atom is expected to behave as

$$E_B = a_V + a_S N^{-\frac{1}{3}}, \tag{1}$$

where the first term is a constant volume term ($a_V < 0$) and the second term reflects the higher energy ($a_S > 0$) of the surface (see also Ref. [5]). Thus, E_B will increase monotonically (in absolute value) with size N for spherical clusters. For elongated structures grown by accretion of a stable subunit the surface-to-volume ratio (which is 1 for the stacked-ring model) remains constant with cluster size, so that E_B is expected to be independent of size. The two dashed lines in Fig. 3 indicate the expected behavior, with parameters that put the curves in the range of calculated energies.

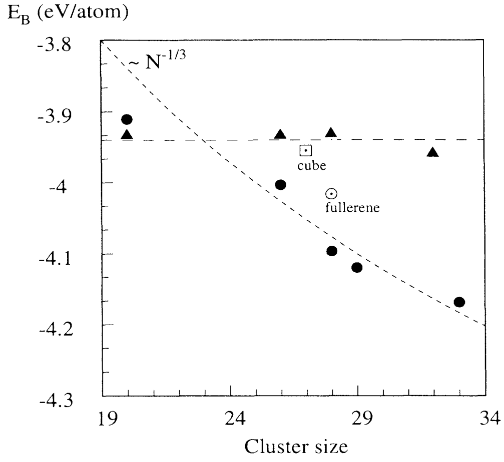

FIG. 3. The calculated binding energy per atom E_B (in eV) for the ring structures (triangles) and the oblate structures (dots) over the size range $N = 20$–33. The square corresponds to the cubic structure of 27 atoms and the circle corrsponds to the 28-atom fullerene structure. The dashed lines describe the expected behavior for spherical clusters ($E_B \sim N^{-\frac{1}{3}}$) and that of elongated shapes (constant E_B).

Let us discuss in more detail the nature of the transition reflected in Fig. 3, in the context of the models considered here. There are two aspects of the cluster shape that bring about the transition. First, both classes of models contain bonding arrangements that are close to the directed covalent bonds characteristic of the infinite-size system (the diamond crystal). The larger compact structures possess the added feature of *surface relaxations* which are close to reconstructions of bulk Si surfaces. This enhances their stability. The relative energies of the different cluster shapes at $N = 20$ and $N = 26$ illustrate this effect. At both sizes, the two types of clusters consist solely of threefold coordinated surface atoms. The dodecahedron structure [Fig. 2(a)] is the smallest compact cluster that we were able to construct, with directed covalent bonds at bond angles (108°) close to the tetrahedral angle (109.4°) of the diamond crystal. However, the very high symmetry (I_h) of this geometry leaves no room for relaxation, and the bonding features characteristic of reconstructed Si surfaces cannot be realized. The energy of this structure is higher than that of the elongated stacked ring structure of equal size [Fig. 1(a)]. The first size where surface-related features appear in the compact class is $N = 26$, which has a ring of dimers on the surface corresponding to the dimer reconstruction of the Si(100)-(2×1) surface. As seen from Fig. 3, the $N = 26$ compact cluster is significantly more stable than the elongated ring structure of equal size, *even though both geometries contain exclusively threefold-coordinated surface atoms.*

The compact shape becomes even more stable when two atoms are added to the interior of the 26-atom clusters to form the 28-atom structures [see Figs. 1(c) and 2(c)]. This observation leads to the second important aspect of the change in shape suggested by the binding energy results: this transition is marked by the emergence of stable interior atoms in the compact structures. For roughly spherical clusters larger than a critical size, there is room in the cluster interior to accommodate covalently bonded atoms. From the models considered here, this critical size appears to be $N = 26$. In contrast, the elongated structures have too small a cross section to accommodate interior atoms. For example, inserting two atoms in the middle of the 26-atom ring structure to produce an elongated structure of 28 atoms [see Fig. 1(c)] does *not* lower the cluster binding energy. Finally, we note that higher coordination alone is not a determining factor in cluster stability. The simple cubic arrangement of 27 atoms is energetically rather unfavorable (see Fig. 3), even though it contains one central sixfold-coordinated atom and all other atoms have coordination 3 or higher (the average coordination is 4). In the same vein, the 28-atom empty-cage fullerene structure, which produces quite stable carbon clusters [15], has higher energy than our model of the same size consisting of two interior Si atoms and a surface of Si dimers [Fig. 2(c)]. This demonstrates the importance of the shape and the bonding arrangement of the surface atoms in producing a low-energy stable structure. The structures with 29 and 33 atoms fulfill all the requirements for optimal bonding: they contain five interior atoms, they have surface features that closely resemble those of reconstructed Si surfaces, and their shape is as close to spherical as possible, while maintaining predominantly covalent bonding. Their low E_B further confirms our conjecture regarding the structure of these systems.

For the elongated clusters, it is certainly possible that other structural units of low energy could be stacked to produce favorable prolate geometries (see Ref. [2]). For the compact clusters on the other hand, we believe that our models may be close to optimal, since they embody a number of features that tend to stabilize bulk and surface structures of Si. If this is the case, any elongated cluster in the size range above $\sim$ 29 will lie higher in energy than our models for the compact clusters. Thus, we expect that when other structures are considered, the constant-energy line in Fig. 3 corresponding to elongated structures could move lower, whereas the $N^{-\frac{1}{3}}$ line corresponding to compact spherical structures is close to its optimal position. These considerations indicate that the crossover between elongated and spherical shapes lies in the range $24 \leq N \leq 28$ (see Fig. 3). The lower bound corresponds to structures with surface atoms only, which leads to predominance of prolate geometries from stacking of stable subunits. The upper bound corresponds to a size at which interior atoms in compact clusters become stable, as our models demonstrate, and the spherical shape begins to dominate. Although this behavior can be surmised on general grounds, our models and total-energy calculations give a detailed understanding of why the transition in shape takes place at the observed range of sizes [1,2]. It is also of interest that this transition in shape is independent of kinetics, since it is observed at the same size for annealed and unannealed clusters [1,2]. This strongly suggests that the transition has to do with a fundamental change in the nature of the cluster geometry (which is captured by the two qualitatively different classes studied here), rather than specific geometrical changes that may depend on kinetics. The appearance of interior atoms and surface-reconstruction features indicates that the transition in shape is related to the development of bulklike features in these clusters, which has been the subject of intense theoretical investigation [3,4,9]. Thus, the present work provides indirect evidence that the critical size N_c for a transition from size-specific behavior (characteristic of very small clusters) to bulklike behavior (characteristic of the infinite system) is also in the same range, $24 \leq N_c \leq 28$.

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