Effect of Surface Reconstruction on Stability and Reactivity of Si Clusters

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It is proposed that "magic-number" Si clusters of intermediate size correspond to structures in which exactly all surface atoms participate in reconstructions similar to bulk-Si surfaces. Models are given for the experimentally observed stable clusters of 33 and 45 atoms, which display features similar to the 7×7 and 2×1 reconstructions of the Si(111) surface. The nature of bonding in the energy-optimized atomic geometries is revealed, through first-principles electronic structure calculations, to be covalent.

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Small clusters of atoms have recently become the subject of intense study in the hope that their properties can provide new insight to the physical and chemical behavior of the parent materials. In particular, the high surface-to-volume ratio in small clusters and their size-dependent reactivity may help shed light on complex processes such as catalysis. Moreover, the flexibility afforded by the small number of atoms could give rise to novel structures, which can possibly lead to the synthesis of artificial materials with uncommon properties.[1] For example, small ($n \leq 10$) clusters of Si exhibit high coordination,[2] in contrast to the tetrahedral bonding of the diamond lattice which characterizes the stable crystalline and amorphous phases. Si clusters of somewhat larger size show dramatic changes in their chemical reactivity, depending on the number of atoms in the cluster.[3] Thus, some clusters (specifically $n=33$, 39, and 45) have reactivity several orders of magnitude lower than their immediate neighbors in size.

In order to elucidate the properties of Si clusters, it is of great importance to develop specific models for their structure. In the case of small ($n \leq 10$) clusters, extensive first-principles calculations have explored the configurational phase space and have identified the lowest-energy structures.[2,4,5] This procedure, however, is not practical for larger sizes: For a system with many degrees of freedom the problem of identifying and sorting the lowest-energy configurations belongs to the class of *NP*-complete problems and quickly becomes computationally intractable as the size increases.[6] Thus, for clusters of intermediate size ($10 < n < 100$), the search for the lowest-energy structure through first-principles calculations is necessarily limited to a subset of the possible configurations and must be guided by physical insight or empirically developed models.[7] It is also reasonable to concentrate on finding models for experimentally observed sizes of exceptional stability (so-called "magic numbers"), which can then serve as paradigms for the structural characteristics of clusters.

In this Letter a new, physically motivated approach to the study of intermediate-size Si clusters is proposed. It is based on the premise that for $n \sim 30$–40 it is possible to construct a network containing a core of fourfold-coordinated atoms, similar to bulk Si, which are surrounded by a surface of atoms with optimal (threefold or fourfold) coordination, similar to Si surfaces. Structures of exceptional stability can be obtained when *exactly all* surface atoms participate in the surface reconstruction and any change in the size (addition or removal of atoms) introduces "defects" similar to those on bulk surfaces. Pursuing this premise, and guided by experimental results, I have constructed two models, containing 33 and 45 atoms, that fulfill all the structural requirements outlined above. These sizes are observed experimentally to have unusually low chemical reactivity,[3] which can be interpreted as an indication of their stability. The most interesting aspect of the proposed models is that *all* surface atoms participate in forming geometric configurations that resemble very closely the two most stable reconstructions (7×7 for the size 33 and 2×1 for the size 45) of the (111) surface which is the cleavage plane (i.e., the lowest-energy surface) of Si.

Perspective three-dimensional views of the Si_{33} and Si_{45} models are shown in Figs. 1 and 2, respectively. In each model there are few physically distinct atomic environments (labeled 0–4 in Si_{33} and 0–5 in Si_{45}). These environments are color coded and only some representative atoms are labeled by numbers. The central atom in each cluster (labeled 0 and colored black) has four neighbors in perfect tetrahedral arrangement. These neighbors (labeled 1 and colored gray) are also fourfold bonded, although their bonds are not at exactly tetrahedral angles due to relaxation. The Si(1) atoms are bonded to three surface atoms each (labeled 2 and colored blue). At this point the similarities between the Si_{33} and Si_{45} clusters end, as the remaining surface atoms are in different positions.

In the Si_{33} cluster, the Si(2) atoms are fourfold coordinated: In addition to their Si(1) neighbor, they are bonded to two other surface atoms labeled 3 (colored green) and one atom which resides directly outward from the Si(1) atom and is labeled 4 (colored red). The latter atom occupies a position similar to the T_4 adatom position in the 7×7 reconstruction of Si(111).[8] Each Si(3) atom is threefold coordinated, with two bonds to Si(2) atoms, and one bond to another Si(3) atom. The relaxation required to form the Si(3)–Si(3) bond is very similar to the atomic displacement in the dimer pairs

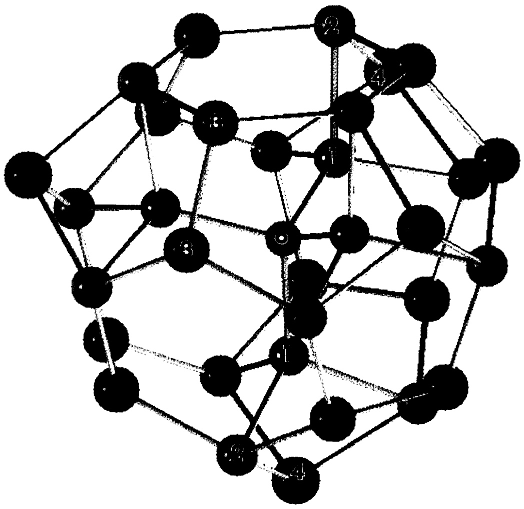

FIG. 1. Perspective view of the Si_{33} cluster. Distinct atomic environments are color coded. Representative atoms in each atomic environment are labeled by numbers. Larger atoms (bright colors) are farther from the center.

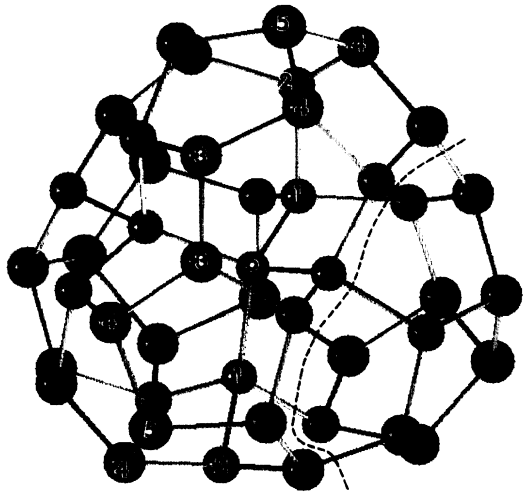

FIG. 2. Same as Fig. 1 for the Si_{45} cluster.

that flank the corner adatoms in the 7×7 reconstruction. Thus, the surface of the Si_{33} clusters is characterized by two of the most important structural features of the 7×7 reconstruction, dimers and adatoms (the 7×7 reconstruction is also known as the dimer–adatom–stacking-fault, or DAS, model). In the proposed model for Si_{33}, the adatoms are flanked by three dimer pairs each, whereas in the 7×7 reconstruction the corner adatoms have only two dimer pairs next to them. However, under proper stress conditions, reconstructions of the same nature (DAS) but with smaller unit cells (5×5 or 3×3) are energetically favored.[9] The 3×3 DAS reconstruction in particular exhibits a very close resemblance to the proposed Si_{33} model, having one T_4 adatom in each half of the unit cell, flanked by three dimer pairs.

The surface of the Si_{45} cluster exhibits features similar to the other stable reconstruction of Si(111), the 2×1 π-bonded chain reconstruction.[10] In this cluster, the Si(2) atoms are threefold coordinated: In addition to their Si(1) neighbor, they have two other neighbors labeled 3 and 4 (both colored green, since these two atomic environments are very similar, though not identical). The Si(3) atoms have one Si(2), one Si(3), and one Si(4) neighbor, whereas the Si(4) atoms have one Si(2), one Si(3), and a third neighbor labeled 5 (colored red). The Si(5) atoms are surrounded by three Si(4) atoms. In this structure, the surface atoms form zig-zag chains composed of (4)-(3)-(3)-(4) sequences and anchored at the four Si(5) apex atoms. There are six such chains spanning the entire surface of the cluster. The stability of the chain structure is due to strong π-bonding interactions between the dangling bonds of the surface atoms, similar to the interactions of dangling bonds which stabilize the Si(111) 2×1 surface.[10]

The close resemblance of the Si_{33} and Si_{45} surfaces to reconstructed bulk-Si surfaces gives a qualitative explanation of the low chemical reactivity of these clusters: it is due to passivation of the surface dangling-bond orbitals by charge-transfer and delocalization interactions similar to those encountered on reconstructed bulk surfaces. Concomitantly, removing or adding atoms to these structures introduces highly reactive surface orbitals, analogous to defect states on bulk surfaces. This results in a sharp increase of the chemical reactivity. A more quantitative explanation, based on the nature of occupied and unoccupied electronic states of the clusters, will be presented elsewhere.[11]

In order to obtain relaxed atomic geometries for the models described above, I have performed extensive energy-minimization calculations. For the case of the Si_{33} cluster, it is feasible to perform these calculations using pseudopotential local-density-functional theory. Thus, the structure of Si_{33} was determined by minimizing Hellmann-Feynman forces, obtained from first-principles calculations. For the Si_{45} cluster, first-principles energy-minimization calculations are intractable due to the larger volume required to accommodate this structure. Instead, I employed several classical interatomic potentials for relaxations of the Si_{45} cluster and used the structures thus obtained as input to the first-principles method in order to arrive at a low-energy geometry (details in Ref. 11).

The optimal geometries are defined by the position of the representative atoms in each cluster, which are given in Table I. The average and the extrema of bond lengths are also included in Table I. The model for Si_{33} possesses perfect tetrahedral symmetry, whereas the model for Si_{45} is symmetric under all the rotational operations of tetrahedral symmetry but does not have reflection-symmetry planes. Thus, the Si_{45} model exhibits chirality: There exist two structures with identical local atomic

TABLE I. Positions of the representative atoms in the Si_{33} and Si_{45} clusters in a.u., with respect to the central Si(0) atom. The average (b_{av}), longest (b_{max}), and shortest (b_{min}) bonds are given, with (%) deviations from the ideal bulk bond length.

	Si_{33}			Si_{45}		
Atom	x	y	z	x	y	z
1	0.000	0.000	−4.135	0.000	0.000	−4.471
2	−4.048	0.000	−6.113	−3.897	−1.143	−6.167
3	−6.962	0.000	2.255	−8.757	−0.538	3.606
4	0.000	0.000	−8.561	−7.035	1.873	−6.441
5				−9.474	0.000	−3.349
b_{av}		4.477 (+0.8%)			4.375 (−1.5%)	
b_{max}		4.732 (+6.5%)			4.470 (+0.6%)	
b_{min}		4.135 (−6.9%)			4.358 (−1.9%)	

configurations which are mirror images of one another, and should have identical physical and chemical properties. Total-energy calculations indicate that these clusters are energetically stable against addition or removal of atoms,[11] and have a binding energy per atom approximately 0.7 eV higher than the cohesive energy of bulk Si (4.7 eV).

First-principles calculations provide information about the electronic charge distribution in these models, shown in Figs. 3 and 4 for Si_{33} and Si_{45}, respectively. For a direct comparison to bulk Si, Fig. 5 displays a charge-density plot on a (110) plane of the crystal, which is terminated at the lower part by a T_4-adatom geometry on a (111) surface. The bulk bonds in Fig. 5 are very similar in nature to the Si(0)−Si(1) bonds in the Si_{33} and Si_{45} models. Bonds between surface atoms in the two clusters are also similar in nature to bulk-Si bonds, as evidenced by the representative Si(3)−Si(3) bonds (see Figs. 3 and 4). These comparisons indicate that the bonding in the proposed models is covalent. This is further supported by the fact that bond lengths in the optimal structures are close (to within a few percent) to the ideal bond length of bulk Si, 4.443 a.u. (see Table I).

The issue of the crossover size at which covalency becomes favored over high-coordination metallic bonding that characterizes small Si clusters has been extensively debated.[4,5,7,12] Indirect estimates of the crossover size, based on extrapolations from bulk phases and crystal fragments, range from 4000 (Ref. 4) to 50.[12] The present study offers an example of a manifestly covalent structure which is a local minimum in energy (the fully relaxed Si_{33} cluster). If this model proves to be the global lowest-energy configuration for the size 33, it will give a *direct* estimate for the crossover size between covalency and high-coordination metallic bonding. The proof of global lowest energy might be provided, e.g., by

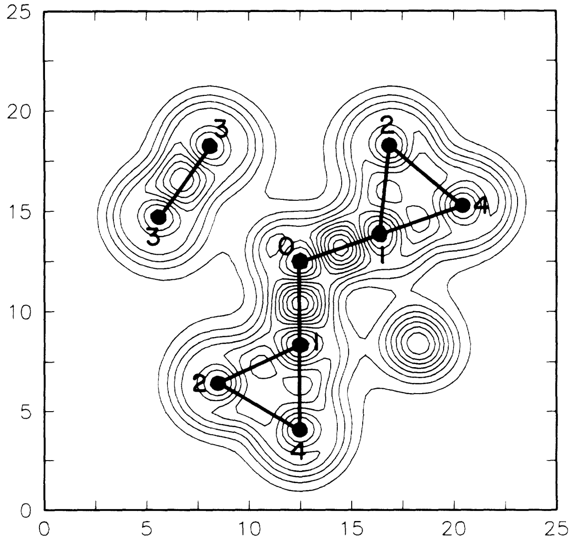

FIG. 3. Valence-electron charge density for the Si_{33} cluster on the x-z plane (refer to Table I). Numbers identify the atoms labeled in Fig. 1.

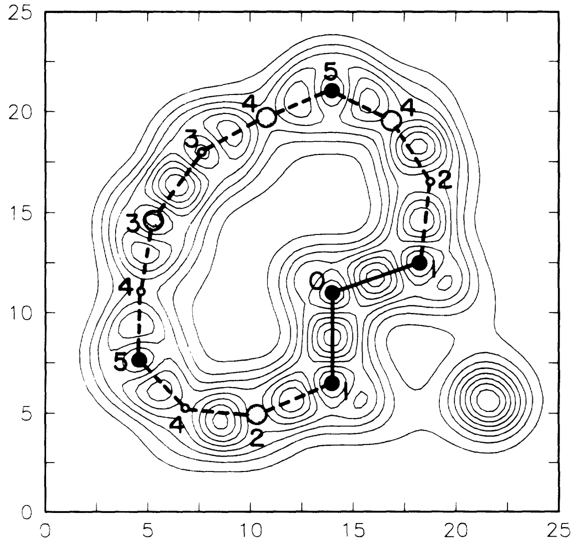

FIG. 4. Same as Fig. 3 for the Si_{45} cluster. Solid circles represent atoms on the plane, shaded larger (smaller) circles represent atoms in front of (behind) the plane. Solid (dashed) lines represent bonds lying on (oblique to) the plane. Numbers identify the atoms labeled in Fig. 2.

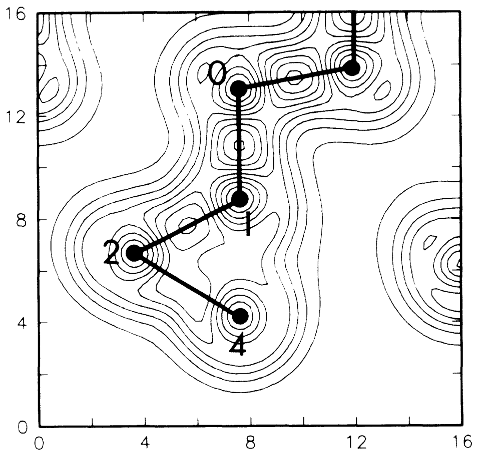

FIG. 5. Valence-electron charge density on a (110) plane of the Si crystal, terminated at the lower part by a T_4-adatom geometry on a (111) surface. Atoms in environments similar to Si_{33} are numbered by analogy to Fig. 3.

molecular-dynamics simulations of "melting" and "recrystallization" of the Si_{33} structure, which are beyond the scope of the present work.

The charge-density plot of Si_{33} reveals an interesting feature of the bonding in this model: The electronic charge density between Si(1) and Si(4) is much higher than between the adatom and the subsurface atom directly underneath it in the corresponding geometry of the crystal surface (compare Fig. 3 to Fig. 5). Accordingly, the Si(1) atoms in the Si_{33} model should actually be considered fivefold bonded and the Si(4) atoms should be considered fourfold bonded. This may be a realization of the fivefold-bonded atom, conjectured by Pantelides to occur in amorphous Si.[13] It appears that the flexibility of the cluster structure allows for this type of bonding, whereas the more constrained crystal surface prohibits a strong fifth bond. The amorphous network is expected to be, at least locally, more flexible than the corresponding crystalline structure,[14] thus making the occurrence of strong fivefold bonds more likely, as in the Si_{33} cluster.

The Si_{45} model can be viewed as a composite of four Si_{10} subunits joined together by the five core atoms. One such subunit, containing one Si(5), three Si(2), three Si(3), and three Si(4) atoms is outlined by a dashed line in Fig. 2. Moreover, the subunit outlined in Fig. 2 can be transformed into a tetracapped octahedron by simple inward relaxation of the Si(2) atoms. The latter configuration has been identified as one of the lowest-energy structures for Si_{10} clusters.[2] Separation of this subunit from the Si_{45} cluster requires the breaking of only six covalent bonds, i.e., a small number of broken bonds per separated atom. These observations are relevant to recent experiments suggesting that fragmentation of Si_{45} may occur preferentially into Si_{10},[15] which lends indirect support to the proposed model.

In summary, I have proposed a new approach to the study of intermediate-size clusters of Si, based on the following premise: The occurrence of magic-number clusters of intermediate size is due to the possibility of forming a surface that closely resembles a stable reconstruction of the crystal, around a core of bulklike tetrahedrally bonded atoms. Specific models were constructed for two clusters of sizes 33 and 45 (observed experimentally to have very low chemical reactivity) with surface features resembling the 7×7 and 2×1 reconstructions of Si(111). Bonding in the proposed models was shown, through first-principles electronic-structure calculations, to be covalent. This could provide the first *direct* estimate of the crossover size ($n_c = 33$) from high-coordination metallic to covalent bonding, if the proposed model for Si_{33} corresponds to a global energy minimum. Further theoretical studies are needed to establish this point. Nevertheless, the proposed models give a natural explanation for the occurrence of these magic numbers (they accommodate exactly the two most-stable surface reconstructions of bulk Si) and for their observed low chemical reactivity (it is due to surface passivation by reconstruction).

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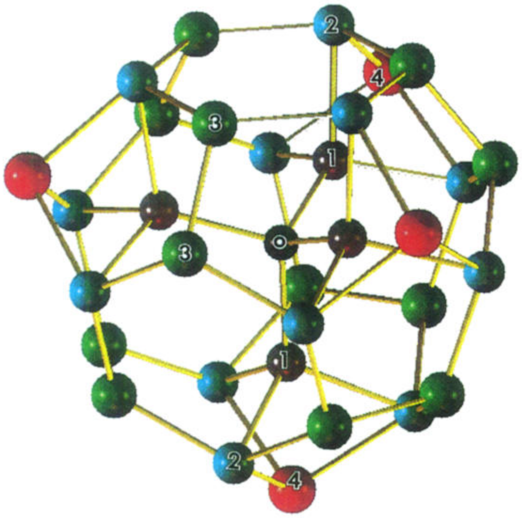

FIG. 1. Perspective view of the Si_{33} cluster. Distinct atomic environments are color coded. Representative atoms in each atomic environment are labeled by numbers. Larger atoms (bright colors) are farther from the center.

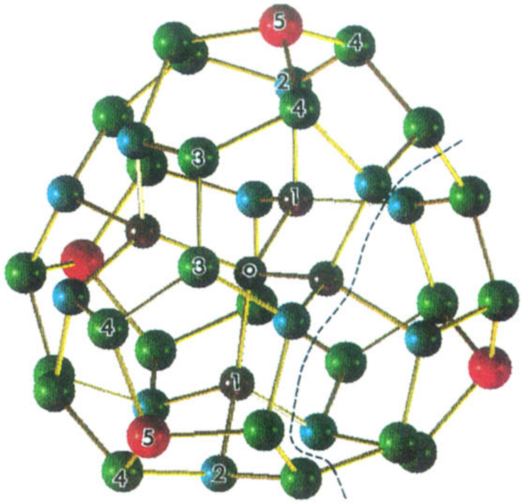

FIG. 2. Same as Fig. 1 for the Si_{45} cluster.