STRUCTURAL MODEL FOR A COVALENTLY BONDED Si_{45} CLUSTER

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A structural model is proposed for a Si cluster of 45 atoms, a size observed experimentally to be chemically non-reactive. The model closely resembles surface reconstructions of bulk Si and consists of a core of fourfold coordinated atoms surrounded by π-bonded chains. The stability of the cluster against addition or removal of atoms was examined through calculations based on interatomic classical potentials. The atomic coordination suggests that bonding in the proposed model is essentially covalent.

1. Introduction

Numerous recent experimental [1–6] and theoretical [7–13] investigations have addressed the properties of clusters of Si, which is a prototypical covalent material. In order to elucidate the existence of so called "magic numbers" (sizes of particular stability), and the dramatically lower chemical reactivity of some cluster sizes [5,14], it is essential to develop specific structural models for these clusters. With the exception of very small clusters (< 10 atoms) for which exhaustive studies have been reported [7,11], structural models are at present lacking. An interesting conjecture for the structure of larger clusters has been proposed by Phillips [9], based on the stability of the sixfold ring in Si.

This Letter was inspired by the work of Smalley and coworkers on the properties of Si clusters of intermediate size (30–50 atoms) [5]. Its purpose is twofold: To propose a new structural model for what is observed experimentally to be a particularly non-reactive Si cluster containing 45 atoms [5,14], and to infer from the features of this model information concerning the bonding characteristics in clusters of this size. In particular, the proposed Si_{45} cluster exhibits structural features almost identical to those encountered in bulk Si surfaces and in this sense its bonding is essentially covalent. The stability of the proposed structure of Si_{45} will be examined through calculations based on interatomic classical potentials (ICPs).

2. Methodology

In investigating the structure of the Si_{45} cluster, we begin with an initial configuration which incorporates well-established knowledge about surface reconstructions of bulk Si. Relaxed structures are obtained using three different ICPs. A representative relaxed structure is then perturbed by removing or adding atoms and the energy of the resulting clusters is compared to the energy of the initial configuration. Thus, the present approach of constructing the model relies mainly on the stability of surface reconstructions of bulk Si. By contrast, in other approaches some method (e.g. molecular dynamics or simulated annealing) is adopted to explore extensively the phase space of possible configurations for a given cluster size. Although this procedure is very efficient in sampling large portions of phase space and gives significant insight to the relative stability of different structures, it runs the following risk: If the lowest-energy structure is a very narrow and deep minimum in the total-energy surface it may be difficult to locate exactly. This might be particularly hard in the case of a structure as highly symmetric as the proposed model for Si_{45}. In addition, for clusters of the size considered here, exploration of the entire phase space is an enormous computational task and may not be feasible even with use of ICPs.

3. Atomic geometry

A three-dimensional perspective view of the model is given in fig. 1. The atoms in this model are shown in different shading and relative size which signifies proximity to the cluster surface. Thus, the lighter the shading and larger the size of the atoms, the farther they are from the center of the cluster. The innermost central atom is shown as black. The cluster has perfect tetrahedral symmetry and is composed of atoms in six different environments (labeled 0 through 5 in fig. 1). For visual clarity, in fig. 1 we have marked by numbers only representative atoms in each environment.

The central atom (labeled 0) is fourfold coordinated, forming four bonds with its nearest neighbors, at exactly tetrahedral angles. The four atoms bonded to Si(0) are labeled 1 and have four bonds, but due to relaxation the angles between these bonds are not exactly tetrahedral. The Si(1) atoms are bonded (in addition to the central atom) to three other atoms each, which are labeled 2. The Si(2) atoms that are bonded to the same Si(1) atom are related to one another by threefold rotational symmetry around the axis defined by the positions of the common Si(1) neighbor and the Si(0) atom. The Si(2) atoms are threefold coordinated; in addition to the Si(1) neighbor they have two other neighbors labeled 3 and 4. The Si(3) and Si(4) atoms are also threefold coordinated. Each Si(3) atom, in addition to its Si(2) neighbor is bonded to another Si(3) atom and to a Si(4) atom. Each Si(4) atom, in addition to its Si(2) and Si(3) neighbors is bonded to another atom labeled 5. Finally, the Si(5) atoms are threefold coordinated surrounded by Si(4) atoms.

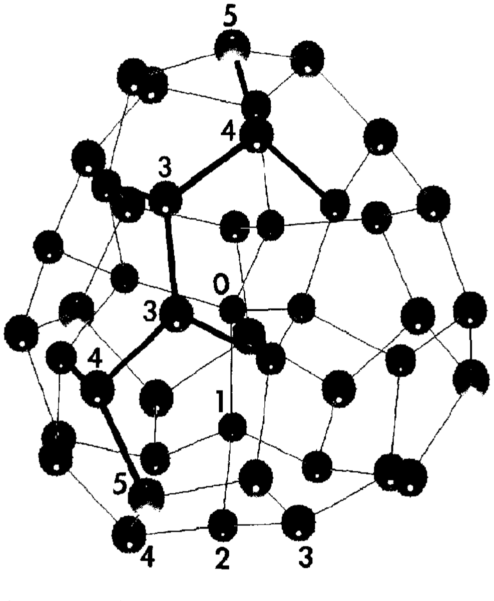

Fig. 1. Three-dimensional perspective view of the Si_{45} cluster. Shading and relative size of atoms indicates proximity to center (lighter and larger atoms are farthest from center). Representative atoms in each atomic environment are labeled 0 to 5. A π-bonded chain through 5–4–3–3–4–5 atoms is highlighted by thicker, darker bonds.

What makes this model particularly appealing are the similarities of its bonding characteristics to those encountered on a real Si surface. Thus the "surface" atoms in the Si_{45} model are all threefold coordinated and the atoms under them (closer to the center of the cluster) are fourfold coordinated, which is the case at reconstructed Si surfaces. Furthermore, the surface atoms are linked to one another in a structure closely related to π-bonded chains [15]. This structure is the prevalent stable feature on the cleavage plane of Si before annealing and gives rise to the (2×1) reconstruction of the Si(111) surface. The π-bonded chains in the Si_{45} cluster are composed of successive Si(4) and Si(3) atoms and are anchored at Si(5) atoms. There are six such chains, spanning the surface of the cluster and meeting at the apex Si(5) atoms. The particular stability of π-bonded chains on the (2×1) Si(111) surface, which is due to strong interactions between surface dangling bonds [15], suggests that the proposed model for Si_{45} should also be stable, since all its surfaces are composed of π-bonded chains.

4. Relaxed configuration

In order to obtain a relaxed atomic configuration for the model just described, we have used three different ICPs for Si [16–18]. The relaxation was performed with a Monte Carlo (MC) algorithm, while maintaining the exact tetrahedral symmetry of the cluster. Thus only five atoms (representatives of Si(1)–Si(5)) were moved at each MC step, and the positions of the symmetry-related atoms were determined by the use of Euler angles and threefold ro-

Table 1
(x, y, z) coordinates (in Å) of the representative atoms with respect to the central atom Si(0). Results are from three ICPs [15–17]. Shortest ($b_{\min}$) and longest ($b_{\max}$) bonds are their percent deviation from the ideal bond length of Si are also included

Atom	(x, y, z) coordinates		
	ref. [16]	ref. [17]	ref. [18]
1	0.00 0.00 −2.39	0.00 0.00 −2.30	0.00 0.00 −2.37
2	0.50 1.84 −3.45	0.50 1.92 −3.43	0.51 2.09 −3.26
3	−0.80 3.43 −2.81	−0.94 3.73 −3.06	−0.94 3.87 −3.05
4	2.52 2.52 −3.13	2.75 2.60 −3.47	2.72 2.73 −3.41
5	0.00 0.00 5.12	0.00 0.00 5.22	0.00 0.00 5.32
$b_{\min}$	2.15 (−8.5%)	2.22 (−5.5%)	2.30 (−2.1%)
$b_{\max}$	2.39 (+1.7%)	2.42 (+3.0%)	2.37 (+0.9%)

tations. The central atom Si(0) was held fixed. At the end of this procedure, the relaxed structure was used as input to an unconstrained MC relaxation, that is, without imposing tetrahedral symmetry. During the unconstrained relaxation only structures of higher energy were found, which indicates that the tetrahedrally symmetric configuration is the lowest-energy structure. Relaxation with the Kaxiras–Pandey potential [16] was thorough (see also section 5), whereas relaxation with the Chelikowsky et al. potential [17] and with the Tersoff potential [18] was less extensive, and is intended only to show that the basic geometry is independent of the ICP choice, within small deviations.

The relaxed Si_{45} cluster is completely determined by the positions of atoms Si(1)–Si(5) relative to the position of Si(0) which is taken as the origin of the coordinate system. These positions are given in table 1, for the three different ICPs used, which give very similar structures: The atomic positions differ by few tenths of an Å at most, and the basic geometric features of the cluster are unchanged. The longest and shortest bonds in each relaxed structure and their percent difference from the ideal bond length of bulk Si (2.35 Å) are also given in table 1. All the bonds are well within the range of covalent bonding in Si, which is about ±10% of the ideal bond length.

5. Total-energy calculations

Having obtained a structure for Si_{45}, we then examined its stability with respect to clusters with more or fewer atoms, obtained from the Si_{45} model by adding or subtracting atoms. The most interesting choices for atoms to be removed or added are those likely to give low-energy structures which can compete energetically with the original Si_{45} cluster. Thus, the atoms which were removed are the outermost Si(5) atoms which are only bonded to other surface atoms, giving the smallest possible disturbance of the cluster. Similarly, the added atoms were placed at positions where they do not destroy the stability of the surface chains, but can potentially increase the cluster stability. These positions are radially outward of Si(1) atoms, and resemble the stable T_4 adatom positions on Si surfaces, such as the 7×7 reconstruction of Si(111) [19]. Placement of adatoms at these positions renders the Si(2) atoms fourfold coordinated and does not otherwise disturb the structure of the original cluster. The adatoms themselves are threefold coordinated, bonded to three Si(2) atoms. Since there are four Si(5) atoms and four adatom positions outward of Si(1) atoms, the range of clusters examined spans clusters from 41 to 49 atoms. Notice that the Si_{41} and Si_{49} clusters also possess perfect tetrahedral symmetry. Once these clusters were defined, their structure was allowed to relax by the same MC procedure used for the Si_{45} relaxation.

For the comparison of energies of different size clusters we used the Kaxiras–Pandey ICP, which has been shown to reproduce reliably the energetics of local distortions and the breaking and forming of covalent bonds in bulk Si [16]. In order to obtain reliable energy differences all MC relaxations with this ICP were thorough. The results of these calculations

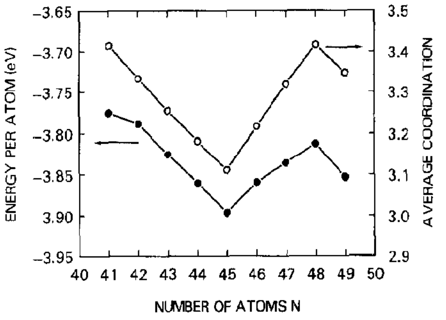

Fig. 2. Energy per atom for various cluster sizes in the neighborhood of the Si_{45} cluster and average coordination as a function of size.

are displayed in fig. 2. The energy curve has a minimum at the Si_{45} cluster. Since the other clusters considered were all obtained from the Si_{45} model, their higher energy per atom demonstrates the stability of Si_{45} *locally* in configurational space. This is sufficient if the Si_{45} model represents a narrow and deep minimum in the total-energy surface, as its high symmetry suggests.

The stability of the Si_{45} cluster is not a result of high coordination. This is illustrated by the average coordination for the different clusters (see fig. 2). The average coordination is defined as the number of nearest neighbors, where nearest neighbor pairs are counted for atoms closer than 2.65 Å. The average coordination is a measure of compactness (high coordination) or openness (low coordination) of the structure. The Si_{45} cluster has an average coordination of 3.111, whereas all other clusters have higher average coordination. This indicates that relaxation of the altered clusters has a tendency to bring atoms closer together and increase their coordination. This, however, does not produce a structure with energy per atom lower than Si_{45}. In this sense the Si_{45} cluster is the most open structure which is a feature characteristic of covalent bonding. By contrast, in structures of high average coordination [7,11], the bonding is usually described as closer to metallic character.

6. Conclusions

The structural features of the proposed model afford some qualitative conclusions about its possible chemical reactivity. The surface of the cluster consists of π-bonded chains similar to those encountered in stable surface reconstructions of bulk Si. Consequently, the chemical reactivity of this model should be comparable to that of the clean (2×1) reconstructed Si(111) surface. Removing or adding atoms from the cluster will create highly reactive dangling bonds on its surface. Thus, the chemical reactivity of clusters obtained from the Si_{45} model through removal or addition of atoms will be significantly higher. However, although the ICP total-energy calculations attest to the stability of the Si_{45} cluster, it is not apparent how this energetic stability can be related to the experimentally observed low chemical reactivity.

The proposed structural model also provides a partial answer to a recently debated question [8,12] about the crossover between metallic and covalent bonding in Si clusters: No more than 45 atoms are needed to construct a cluster with apparently covalent bonding, consisting of a core of fourfold tetrahedrally bonded atoms and surfaces with stable π-bonded-chain reconstructions. This size is very close to the crossover estimate of Chelikowsky [12] (50 atoms), which was based on extrapolation of crystal-fragment energies. The structural model discussed here complements the arguments of Chelikowsky [12] in an essential way by providing a specific example of a cluster with the expected bonding characteristics. This model also supports the conjecture of Phillips that surface-dangling-bond interactions play a dominant role in the structure of clusters [9] (these interactions are optimized in the π-bonded chain configuration [15]).

Another interesting aspect of the model is that a subunit consisting of 10 atoms may be detached from the cluster by breaking only 6 covalent bonds. This subunit consists of an apex Si(5) atom, its 3 Si(4) neighbors and their 6 Si(3) and Si(2) neighbors. Furthermore, inward relaxation of the Si(3) and Si(2) atoms of the detached subunit, immediately leads to the tetra-capped octahedron which is one of the lowest-energy structure for Si_{10} clusters [10]. These observations are particularly interesting in light of experimental evidence suggesting that fragmentation of Si_{45} may occur preferentially into Si_{10} subunits [14].

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