Are Quasi-One Dimensional Structures of Si Stable?

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The stability of quasi-one-dimensional structures of Si is investigated using a generalized tight-binding molecular-dynamics scheme. Our results show that these structures can be stable provided that their geometries consist of a core of fourfold coordinated atoms, surrounded by a threefold coordinated outer surface incorporating one of the most stable reconstructions of bulk Si. Recent experimental works reporting on the synthesis of Si nanowires support these findings.

Silicon based materials have been the focus of extensive research due to their technological importance. Most of these studies have concentrated on either the three-dimensional or cluster forms of Si. The latter form has attracted more interest lately as a result of the experimental findings that indicate the reactivity rates to show considerable variation with cluster size [1]. In particular, Si_{25}, Si_{33}, Si_{39}, and Si_{45} have been found to be least reactive. This has led several groups to propose various physically motivated structures as possible ground state geometries for these clusters [2–7]. An underlying theme among many of these geometries is the presence of a bulklike core surrounded by a reconstructed bulk Si surface [2–5]. Molecular dynamics methods based on the density functional theory in the local density approximations [6] as well as on the generalized tight-binding scheme [7], however, found all these structures to be unstable distorting to geometries with no particular symmetries. More recently, ionization studies were reported for medium size Si clusters [8].

In contrast, quasi-one-dimensional (QOD) aspects of Si based materials have not been investigated in detail. This is due to the difficulty encountered in synthesizing such materials. New forms of stable silicon may offer new materials of technological importance. In particular, presence of direct band gap in the visible region will allow application in light-emitting devices with low power consumption.

In this Letter we propose a novel, physically motivated approach supported by a quantum molecular dynamics method to the QOD structures of Si. We base our approach on the premise that, while in small and intermediate size clusters it may not be possible to have robust structures containing a core of fourfold coordinated atoms, surrounded by an outer surface of atoms with threefold coordination, extended structures can be made stable by the saturation of dangling bonds in at least one direction. The models proposed for the QOD geometries for Si can be broadly categorized into three distinct classes with various degrees of surface to bulk ratio of atoms. All the structures proposed have been fully optimized without any

symmetry constraints using a quantum molecular dynamics method.

The theoretical method used in the present work is the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy [9] that allows for full relaxation of covalent systems with no symmetry constraints. This method has been applied to obtain equilibrium geometries for small silicon clusters [9], in good agreement with *ab initio* results [10]. GTBMD has also been found reliable in obtaining good agreement with experimental results for structural and vibrational properties of Si in the bulk diamond phase [9]. All geometries considered in this work were carefully relaxed to structures that are true local minima of the total energy. The vibrational frequencies were then computed for these relaxed structures within the GTBMD scheme [11] as a further check for stability. None of the structures proposed here had any imaginary frequencies, indicating them to be true local minima of the total energy. Henceforth, in this work the term "locally stable" would indicate absence of any imaginary frequencies.

The building blocks for class 1 QOD structures are multiply connected "superatom" clusters with D_{nh} symmetry with a small hollow region in the middle. Shown in Fig. 1a is a representative with D_{6h} symmetry. This superatom cluster contains 84 atoms and can be visualized as consisting of six circularly connected closed units of 14 atoms each with faces composed of pentagons and hexagons, with sixty of these atoms having threefold coordination. The remaining atoms in the unit are all fourfold coordinated. All outer surface atoms participate in forming geometric configurations that resemble very closely the surface of bulk Si. The bonding of the atoms at the top and the bottom, along the symmetry axis, to their three neighbors resembles the unreconstructed (111) surface of Si. The atoms on the surface farthest from the symmetry axis form dimers as a result of the 2×1 reconstruction; the unreconstructed surface resembling the (100) surface of Si. It is now well known that on Si(100) surface atoms reconstruct to buckled dimers and that on the same row neighboring dimers have same or opposite buckling
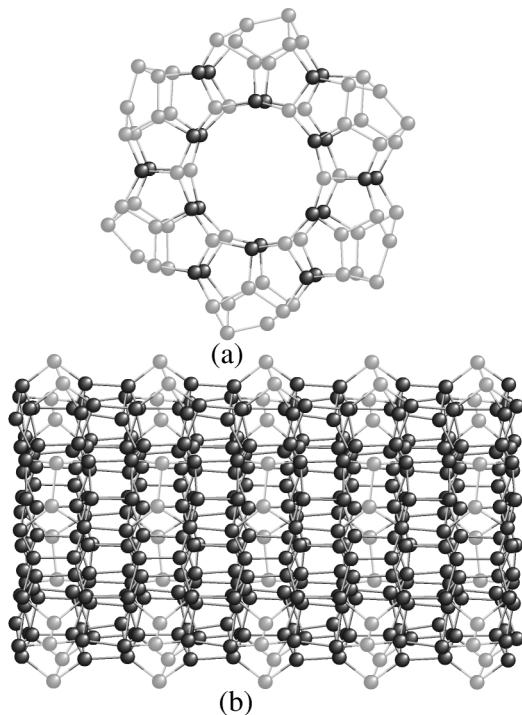
FIG. 1. (a) The superatom cluster containing 84 atoms (D_{6h} symmetry). Surface reconstruction results in the formation of symmetric tilted dimers. All threefold coordinated atoms are shaded light. (b) A section of QOD Si (class 1) structure obtained by stacking the superatom units on top of each other and performing GTBMD relaxation. The ends of the segment show (111) features.

(symmetric/asymmetric dimer configuration) [12–14]. This buckling lifts the degeneracy of the two half-filled dangling bond states of an untilted dimer and results in the opening of a gap at the Fermi level. Molecular dynamics relaxations starting with an untilted configuration resulted in the formation of asymmetric tilted dimers. The symmetric tilted dimer configuration shown in Fig. 1a is found to be isoenergetic with the asymmetric case. As seen in the figure, the surface dimers are all aligned along the circumference.

The QOD structures are obtained by stacking these clusters along the symmetry axis (Fig. 1b). The stacking results in fourfold coordination for all the (111)-type atoms as they form bonds with similar atoms on neighboring unit cells. It is worth noting that (111) surfaces have the lowest surface energy among all other surfaces of Si. The surface dimers, however, remain threefold coordinated and do not form bonds with atoms in the neighboring unit cells. The surface dimers each have a bond length of 2.49 Å, while other bond lengths range from 2.30 to 2.46 Å. Bond angles range from 96° to 126°.

The spacing between the unit cells was obtained by GTBMD relaxation incorporating a constant pressure ensemble [15]. A set of regularly spaced eight k-points

was sufficient to obtain a converged value of 6.14 Å for the lattice constant along the symmetry axis. The wirelike geometry thus obtained is found to be locally stable. Other class 1 QOD structures of D_{nh} symmetries with $n \neq 6$ can be constructed using the prescription given above.

An interesting observation can be made of these QOD structures. The stacking produces "neck" regions with Si-Si bonds parallel to the symmetry axis. These regions facilitate bending of these elongated structures.

The class 1 structures can also be used to derive two widely differing classes of QOD structures with similar structural properties (fourfold coordinated atoms in the interior and threefold on the outside). In one case (class 2), we consider stable structures with larger surface to bulk ratio, having more resemblance to carbon nanotubes. In the other case (class 3), we consider structures with the smaller surface to bulk ratio, more akin to the diamond phase of Si. The superatom units for these classes of QOD structures are shown in Figs. 2a and 2b, respectively. The wirelike structures generated by stacking these clusters are also locally stable, although slightly higher in energy (by 0.34 eV and 0.1 eV/atom, respectively) when compared to the class 1 structures. The QOD structures built from the unit shown in Fig. 2a, consisting of 60 atoms, are obtained by removing outermost dimers from the class 1 structures and relaxing the resulting structure with GTBMD. The relaxation produces several new bond formations in the region farthest from the axis resulting in new dimer formation. The surface dimers each have a bond length of 2.26 Å, as seen in Fig. 2a, and are aligned along the symmetry axis with neighboring dimers having opposite buckling (asymmetric dimer configuration). Other bonds in this structure range from 2.36 to 2.45 Å while the bond angles range from 90° to 144°.

The superatom unit cluster shown in Fig. 2b, consisting of 90 atoms, is obtained from a class 1 unit structure by adding a ring of six Si atoms around the symmetry
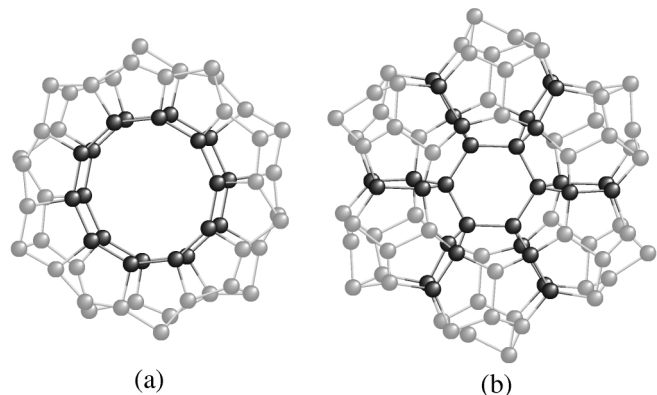

FIG. 2. Superatom cluster units for QOD structures belonging to (a) class 2 and (b) class 3. All threefold coordinated atoms are shaded light.

axis in the center. The GTBMD relaxed QOD structure contains surface dimers each with a bond length of 2.38 and aligned along the circumference. Other bond lengths range from 2.35 to 2.40 Å. The bond angles range from 84° to 120°.

The relatively large bond lengths for the threefold coordinated atoms belonging to classes 1 and 3 may seem counterintuitive; in crystalline Si the surface atoms tend to have shorter bond lengths when compared with the core atoms. A careful examination, however, reveals this "anomalous" increase in the bond length for surface dimers to be due to the strain caused by the alignment of dimers along the circumference. This is substantiated by the observation of "normal" bond lengths for the surface dimers of class 2 structures where they are aligned along the symmetry axis and, therefore, not subject to strain. Since the only surface reconstruction for these QOD structures are the 2×1 type, we expect the surfaces to be at least as reactive as those of the bulk 2×1 surface. The passivation of the surface dangling-bond orbitals through reconstruction is believed to lead to low reactivity [2]. It should be noted, however, that strained bond angles will be more reactive than less strained species. Structures belonging to classes 1 and 3 contain more strained surface bonds than class 2 structures and, consequently, are expected to be more reactive. The bulk surfaces are prone to attacks by oxygen and hydrogen, and we expect these structures to be even more vulnerable. We also note that class 1 structures are 0.45 eV/atom less stable than the bulk diamond structure of Si.

In Fig. 3 we show the local densities of states for the structure in Fig. 2b obtained using a sp^3s^* tight-binding model [16] that correctly reproduces the band gap for bulk Si in diamond structure. The density of states shows a gap of 0.84 eV, slightly smaller than that for bulk Si. Detailed analysis of the band structure using the same tight-binding model revealed the gap to be direct. Similarly, gaps for classes 2 and 3 were also found to be direct and close to 1 eV. The direct band gap obtained for these QOD structures may have important technological implications for making light-emitting devices with low power consumption. Furthermore, presence of large interstitial regions in all these nanostructures may make doping with group III or V elements relatively easy. This may prove to be an important advantage in device fabrication.

In summary, we have proposed novel QOD structures of Si whose surfaces closely resemble one of the most stable reconstructions of the crystalline Si with a core of bulklike fourfold coordinated atoms. It should be noted, however, that these Si structure cannot be extrapolated directly from 3D or 2D Si systems due to strong relaxation effects. Even though we considered many possible structures, only the structures proposed in this work had all nonimaginary frequencies and, therefore, were stable when vibrational analysis was performed.
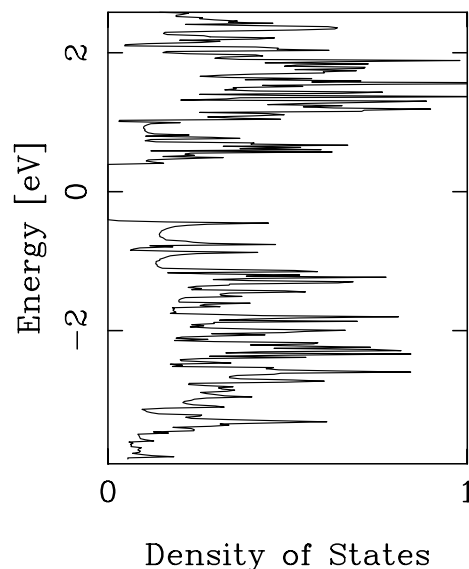

FIG. 3. Electronic density of states for the QOD Si structure in Fig. 1b. The density of states shows a gap of 0.84 eV.

Interestingly, successful synthesis of Si nanowires using a new method of laser ablation has been reported very recently [17,18]. These nanowires were reported to have fairly uniform diameter and frequent bending. The morphology observed in the experiment suggests the growth of these wires to take place along the (111) direction. Furthermore, nanowires were observed to be coated with a sheath of silicon oxide. All these observations support the results reported in this Letter.

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