

# Structure and stability of SiC nanotubes

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We propose structural and electronic properties of recently synthesized SiC nanotubes. The nanotubes with a Si to C ratio of 1:1 exhibit rich morphologies and are shown to belong to two distinct categories that are close in energies but show significant differences in electronic and transport properties. Similarities and differences are invoked with the case of BN nanotubes to explain the observed surface reconstruction.

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The discovery of carbon nanotubes by Iijima<sup>1</sup> has set off a tremendous explosion in general interest in these quasi-one-dimensional structures. Although most carbon nanotubes observed tend to be multiwalled with spacing between the walls close to interplanar distance in graphite, single-walled carbon nanotubes (SWCN's) are also abundantly being produced in experiments, thanks to the recent advances in experimental techniques. SWCN's consist of rolled-up graphene sheets and are predicted to have extraordinary electrical properties.<sup>2</sup>

The successful synthesis of nanotubes made from boron nitride<sup>3–5</sup> has opened up the possibility of the existence of tubular structures made of either noncarbon or part carbon materials. It should be noted that C, B, and N are elements belonging to the second row of the Periodic Table. The small covalent radius of these elements can generate considerable strain energy preventing the formation of close-packed structures with larger coordination found in clusters of covalent elements with larger radii such as silicon. Consequently, C and BN can form very stable low-dimensional structures with smaller coordination. By contrast, low coordinated structures of Si, graphitic or cagelike, are predicted to be unstable.<sup>6,7</sup> The possibility exists, however, that a substitutional doping of tubular Si structures by sufficient number of C atoms may render it stable. This is because both C-C and Si-C bonds are known to be stronger than the Si-Si bond and can counteract the instability in nanotubes containing only Si-Si bonds.

Indeed, very recently, Sun *et al.* have reported the synthesis of silicon carbide nanotubes produced via the reaction of Si with carbon nanotubes.<sup>8</sup> In their work different silicon-carbon nanostructures were synthesized by decomposing SiO on multiwalled carbon nanotubes (MWCN's), used as templates, in different temperature zones. These structures included  $\beta$ -SiC nanowires and biaxial SiC-SiO<sub>x</sub> nanowires.

But more importantly, they reported the observation of SiC nanotubes for the first time. The SiC nanotubes were formed through a substitutional reaction with Si atoms replacing half of the C atoms in the MWCN's with the new structure containing a Si to C ratio of 1:1. Even though the nanotubes were multiwalled, they differed significantly from the MWCN geometries in that the interplanar spacings were significantly larger than the 3.4 Å typically observed for MWCN. The spacings in many cases were found to be as large as 4.5 Å indicating very loose coupling between the layers. This suggests that each layer can be taken to be independent of others and considered to be a single-wall SiC nanotube. The precise geometry of the layers was not determined, however, in experiments. A detailed investigation of the structural properties of these newly synthesized SiC materials is, therefore, timely and useful.

In this work we investigate the structure and stability of various SiC nanotube structures using the generalized tight-binding molecular-dynamics (GTBMD) scheme of Menon and Subbaswamy and *ab initio* methods. Our calculations show two distinct geometries for each chirality to be highly stable. The GTBMD method allows full structural relaxation with no symmetry constraints and has been used extensively in the study of carbon fullerenes and nanotubes.<sup>9</sup> The method has also found success when used in the case of BN nanotubes.<sup>10</sup> The prediction based on the GTBMD scheme that zigzag chirality should be the most stable form for BN nanotubes<sup>10</sup> was confirmed by experiments shortly thereafter.<sup>11</sup> More recently, the method has been successfully applied to the study of small size Si<sub>m</sub>C<sub>n</sub> clusters and SiC heterofullerenes.<sup>12,13</sup> The infinite systems are simulated using a *k*-space supercell formalism incorporating a constant pressure (“movable wall”) ensemble.<sup>14</sup> This allows for a simultaneous relaxation of lattice and basis degrees of freedom. A uniform grid consisting of 126 *k* points was used in the calculation of forces. The infinite two-dimensional (2D)

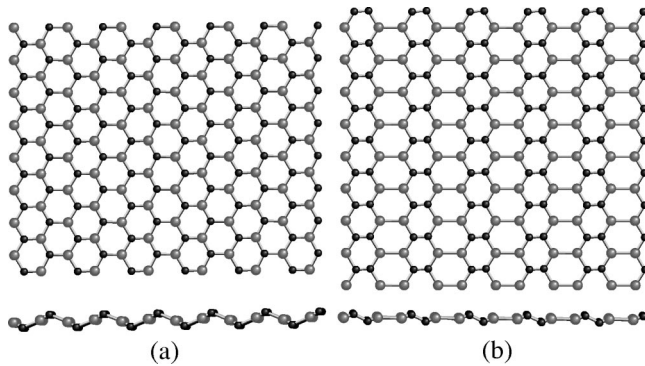


FIG. 1. (a) Type-1 and (b) type-2 graphene sheets of SiC with Si to C ratio of 1:1 obtained by GTBMD relaxation. The surface reconstruction results in wavelike appearance. The top and bottom panels in each of these figures show top and side view of the structures, respectively. In both structures Si atoms (colored grey) are all in a single plane, while C atoms (colored black) are displaced above and below this plane.

graphene sheet used in the calculations is simulated using a 128 atom supercell, while the infinite nanotube is simulated using a 192 atom supercell. In the *ab initio* calculations we use density-functional theory method in the cluster approximation (real-space approach) as implemented in the GAUSSIAN program package.<sup>15</sup> Hydrogen atoms were attached to the edge atoms to passivate all dangling bonds. Structural optimizations were then performed for all the structures using the *ab initio* method. The computational demands imposed by the *ab initio* methods, however, caused us to limit the system size to a maximum of 72 atoms.

Since carbon nanotubes are obtained by rolling up graphene sheets, we begin our study by first investigating stable SiC graphene structures. In Fig. 1 we present two infinite 2D planar structures that were obtained to be local minima using the GTBMD method. Each of these structures contains a Si to C ratio of 1:1. The hexagonal network in Fig. 1(a) consists of alternating Si and C atoms with each Si atoms having as nearest neighbors only C atoms and vice versa. We call this type-1 SiC graphene sheet. Another arrangement is obtained when the nearest neighbors of each Si atom consist of two C atoms and another Si atom as shown in Fig. 1(b). We call this type-2 SiC graphene sheet. The top and bottom panels in each of these figures show top and side view of the structures, respectively. As seen in the bottom panels, the structures are not entirely planar but exhibit wavelike or “rippled” features. In type-1 structure, while the Si atoms are all in a single plane, the C atoms in alternate rows are displaced above and below this plane, respectively. The situation is similar in type-2 structures also with all Si dimers arranged in a plane and the C dimers rotated out of the plane with alternate rows of C atoms displaced above and below this plane, respectively. Our *ab initio* calculations show type-1 structures to be more stable than type-2 structures by 0.43 eV per SiC atom pair.

Single-wall SiC nanotubes with a Si/C ratio of 1 can be constructed by rolling up type-1 and type-2 graphene sheets. In Fig. 2 we show nanotubes obtained from type-1 graphene sheet. All structures are fully relaxed without any symmetry

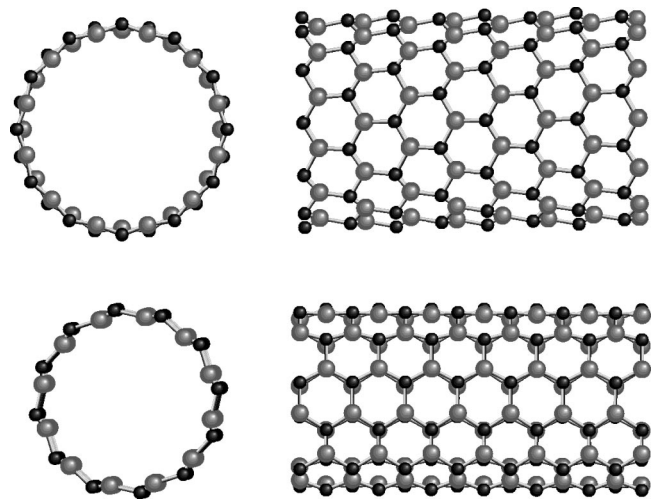


FIG. 2. Single-wall SiC nanotubes of zigzag (top panel) and armchair (bottom panel) chirality obtained by rolling up the graphene sheet in Fig. 1(a) and performing GTBMD relaxation.

constraints using the GTBMD scheme. The top panel shows view along the axis of symmetry as well as side view for the zigzag arrangement of Si and C atoms. The bottom panel shows the two views for the armchair arrangement of atoms. Using the standard chiral vector notation ( $n,m$ ) used for carbon nanotubes<sup>2</sup> these denote (12,0) and (6,6) nanotubes, respectively. As shown in the figure, the Si atoms and C atoms arrange themselves in two concentric cylinders with all Si atoms forming the inner cylinder and all C atoms forming the outer cylinder. This reconstruction is reminiscent of that seen for BN nanotubes where the more electronegative N atoms rotate outward and more electropositive B atoms move inward resulting in a rippled surface.<sup>10</sup> Our *ab initio* calculations show both structures to be stable. The total energy calculations using *ab initio* methods reveal the armchair (6,6) SiC nanotube to be slightly more stable than the zigzag (12,0) SiC nanotube (by 0.05 eV per SiC atom pair). This is in striking contrast to the case of BN nanotubes where the zigzag arrangement is found to be more stable than the armchair arrangement.<sup>10,11</sup> By contrast, carbon nanotubes show no surface reconstruction and all chiralities are equally preferred.

The single-wall SiC nanotubes formed by rolling up type-2 graphene sheet are shown in Fig. 3. The resulting (12,0) zigzag nanotube (top panel) shows rippled surface on GTBMD relaxation with Si and C atoms forming cylinders of different radii. As can be seen in the figure, the outer cylinder is populated by the C atoms and the inner cylinder by the Si atoms. While the displacement directions for Si and C atoms in the (12,0) nanotube are the same as in the case of both zigzag and armchair nanotubes formed by rolling up type-1 graphene sheet, an entirely different displacement pattern is seen for the (6,6) armchair nanotube obtained from type-2 graphene sheet. As seen in the bottom panel of Fig. 3, the structure is highly distorted with all Si dimers arranged along the tangent to the circumference of the nanotube and the C dimers rotated away from the tangent. The origin of high strain can be understood by examining the type-2 graphene sheet shown in Fig. 1(b). The sheet consists of two

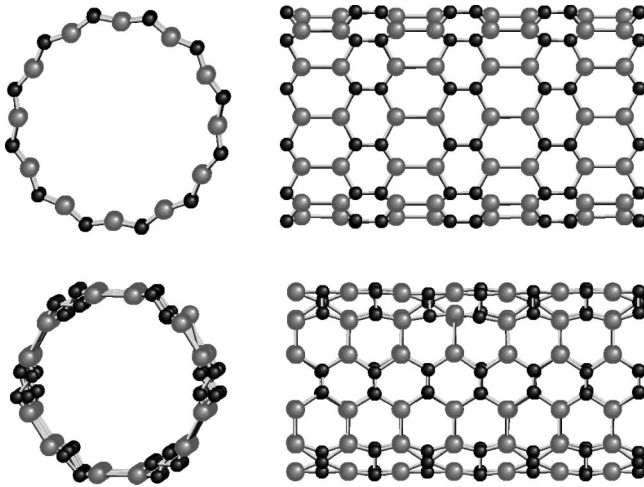


FIG. 3. Single-wall SiC nanotubes of zigzag (top panel) and armchair (bottom panel) chirality obtained by rolling up the graphene sheet in Fig. 1(b) and performing GTBMD relaxation.

types of imperfect hexagons. Rolling up this sheet to form a zigzag nanotube (top panel in Fig. 3) results in the alignment of all Si-Si and C-C dimers along the axis of symmetry with minimal strain on the bonds. When the sheet is folded to form an armchair nanotube (bottom panel in Fig. 3), however, there is a “bending” of Si-Si and C-C dimer bonds. For the short C-C bond, this results in considerable strain. This strain, obviously, is inversely related to the diameter of the nanotube. This strain is further compounded by the rotation of the C-C dimers. Not surprisingly, our *ab initio* calculations show the zigzag (12,0) SiC nanotube (top panel Fig. 3) to be more stable than the armchair (6,6) SiC nanotube (bottom panel in Fig. 3) by 0.45 eV per SiC atom pair. This is very similar to the armchair BN nanotube case where the strain caused by the bending of the B-N bonds causes it to be less stable than the corresponding zigzag case.<sup>10,11</sup>

In Table I we summarize our results for bond lengths and relative energies. Note that while the GTBMD calculations were performed on infinite SiC nanotube systems, the *ab initio* calculations were performed on H passivated finite SiC clusters. This is why we get a bond-length distribution rather than fixed Si-Si, Si-C, and C-C bond lengths in the *ab initio* calculations. The only exception being the type-2 armchair (6,6) SiC nanotube where considerable distortion caused by the strain of C-C bond bending and bond rotation results in a

range of bond lengths, even for the infinite system. The table suggests type-1 SiC nanotubes to be more stable and, therefore, more easily produced in experiments. However, type-2 zigzag SiC nanotube is only slightly higher in energy, and may be produced in experiments under favorable thermal conditions. Furthermore, the energy differences between all structures considered are expected to diminish with an increase in the diameter of the nanotubes, making the production of all structures plausible for large diameter values.

It is instructive to compare the stabilities of SiC nanotubes proposed here in the light of known results for BN nanotubes. Only alternate B-N arrangement is known to exist for the BN nanotubes. This is because of the exceptional stability of B-N bonds. While the zigzag BN nanotubes have been determined to be more stable than armchair BN nanotubes,<sup>10,11</sup> in the corresponding SiC case (i.e., for type 1) the two chiralities are almost isoenergetic with the armchair nanotube being slightly more stable. In the case of BN nanotubes, the lesser stability of armchair nanotubes can be explained by the strain of B-N bond bending resulting from folding the BN graphene sheet to form the armchair nanotube.<sup>10</sup> Even though the same mechanism may be invoked in the case of type-1 SiC nanotubes it should be noted that the Si-C bond length is larger than the B-N bond length. Consequently, the strain associated with bond bending is reduced. In type-2 SiC nanotubes, however, the C-C bond lengths are comparable to B-N bond lengths and the strain resulting from bond bending and bond rotation makes the armchair nanotubes less stable, just as in the case of BN nanotubes.

Since the 3D bulk SiC systems are known to be wide band-gap materials,<sup>16</sup> it is instructive to see how the electronic properties of these new materials change in going to lower dimensions. In Fig. 4 we show the local densities of states (DOS) for the SiC nanotubes in Figs. 2 and 3 using the GTBMD scheme. The top and bottom panels in Fig. 4 show DOS for the zigzag and armchair SiC nanotubes, respectively. While type-1 SiC nanotubes show large band gaps (3.23 eV and 3.53 eV for top and bottom panels, respectively), similar in values to the 3D bulk SiC systems [3–3.3 eV (Ref. 16)], significant reductions in band gaps are seen for type-2 nanotubes (0.7 eV and 0.5 eV for top and bottom panels, respectively). We note that the gap values for type-2 SiC nanotubes are very close to those of carbon nanotubes.

TABLE I. Relative energies per SiC atom pair and bond lengths for the SiC nanotubes shown in Figs. 2 and 3.

Structure	Energy (eV)	Bond lengths (GTBMD)			Bond lengths ( <i>ab initio</i> )		
		Si-C (Å)	Si-Si (Å)	C-C (Å)	Si-C (Å)	Si-Si (Å)	C-C (Å)
(12,0), type-1	0.54	1.87			1.77–1.85		
(6,6), type-1	0.49	1.87			1.79–1.80		
(12,0), type-2	0.92	1.87	2.31	1.51	1.82	2.30	1.47
(6,6), type-2	1.37	1.87	2.31	1.44–1.53	1.82–1.85	2.27	1.43–1.44
Graphitic, type 1	0.0	1.86			1.77–1.81		
Graphitic, type 2	0.43	1.86	2.30	1.41	1.78–1.81	2.25–2.28	1.41–1.47

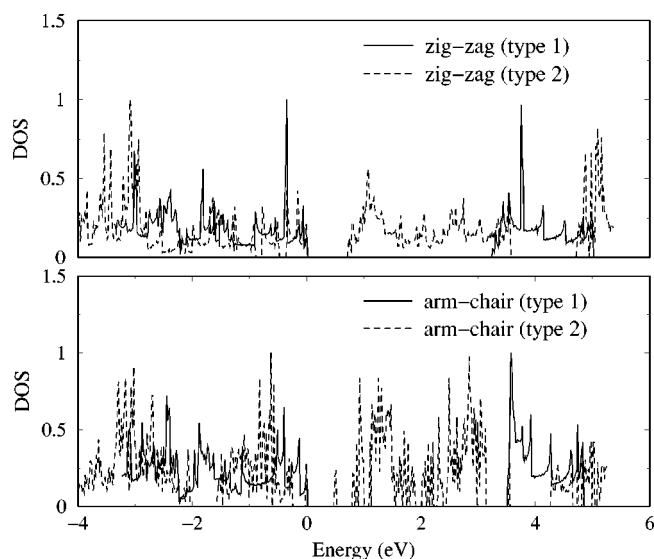


FIG. 4. Densities of states (DOS) for the zigzag (top panel) and armchair (bottom panel) showing reductions in the gap for type-2 SiC nanotubes.

The significant differences in the band gaps for the two types of SiC nanotubes are also reflected in the  $I$ - $V$  characteristics of these nanotubes. In Fig. 5 we present the calculated  $I$ - $V$  curves for the two armchair (6,6) SiC nanotubes. These curves were obtained under a symmetric bias condition using the recently proposed transfer Hamiltonian approximation (THA) method<sup>17</sup> incorporating the applied bias-voltage self-consistently (to be referred to as the SC-THA method). According to this SC-THA scheme, the applied voltage is assumed to be changing linearly from one end of the nanotube to the other. For each value of the bias voltage the Fermi energy of the system is calculated, thereby achieving a zeroth order of self-consistency. The SC-THA method uses the same tight-binding Hamiltonian as used in the

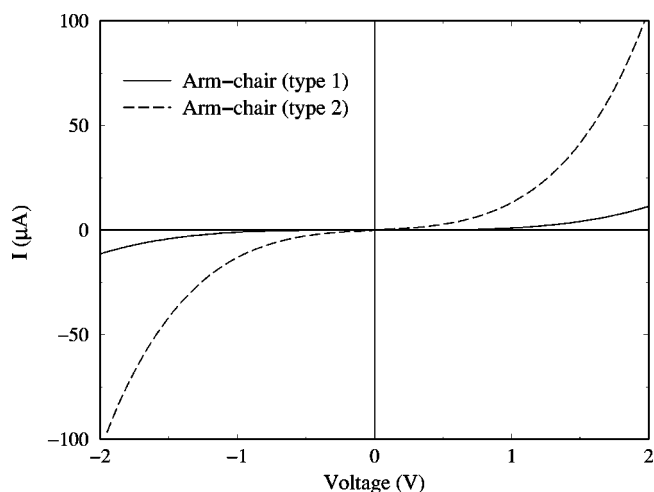


FIG. 5. Current vs voltage ( $I$ - $V$ ) characteristics of the two types of armchair SiC nanotubes showing a significant enhancement in currents for type-2 nanotubes.

GTBMD structural relaxation for the SiC nanotubes. As seen in Fig. 5, the energy gaps are reflected in the  $I$ - $V$  curves making the current values significantly larger in the case of type-2 SiC nanotubes for the same voltage values.

In summary, we have presented structural and electronic properties of two distinct types of stable SiC nanotubes with a Si to C ratio of 1:1. While these two types of nanotubes are close in energy, with type-1 predicted to be more stable, their band-gap values are significantly different. This could have important technological implications in the field of band-gap engineering.

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