

Ab initio calculations for a hypothetical material: Silicon nanotubes

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Electronic and structural properties of a hypothetical material, silicon nanotubes, are examined through first-principles calculations based on density functional theory. Even considering that Si nanotubes have never been observed, this paper attempts to establish the theoretical similarities between Si and C, like band structures and density of states, as well as the main differences, especially associated with cohesive energies. The band-structure calculations for silicon nanotubes show that, similar to carbon structures, depending on their chiralities, they may present metallic (armchair) or semiconductor (zigzag and mixed) behaviors.

In the last few years, nanotubes have aroused great excitement due to their unique physical properties, which span a wide range, from structural to electronic.¹ The interest is about new observed materials and also over hypothetical ones. For instance, the fact that the conductivity properties of carbon nanotubes depend drastically on both the diameter and the chirality of the hexagonal lattice along the tube was predicted theoretically by Mintmire *et al.*,² who had already performed electronic band-structure calculations before the experimental discovery of single-wall carbon nanotubes was even disclosed.

In general words, the common explanation as to why only carbon makes bucky ball structures and silicon does not is the fact that the sp^2 hybridization is more stable in carbon, whereas the sp^3 hybridization is more stable in silicon.³ This is reflected in graphite being the most stable crystal structure for C, whereas for Si it is the diamond structure. Also, for small clusters, C makes linear chains [one dimensional (1D)] and 2D-like clusters, whereas Si makes more compact 3D-like clusters.⁴

However, even though no Si tube has ever been observed, and despite the above-mentioned difficulties in having an sp^2 -like structure for Si, it is interesting to compare the electronic and structural properties of a hypothetical Si nanotube with those of a C nanotube, and also see how unfavorable the Si nanotube is with respect to the most stable diamond structure. Moreover, given the technological importance of silicon, it is justifiable to study such a material, even if only at a speculative level.

The adopted *ab initio* calculation⁵ is based on the density-functional theory within the local density approximation.⁶ We use a norm-conserving pseudopotential in fully separable form⁷ for the treatment of the valence-electron ion-core interaction. The Kohn-Sham equations are solved using the Car-Parrinello scheme,⁸ with the exchange correlation term taken in Ceperly-Alder form as parametrized by Perdew and Zunger.⁹ A plane-wave basis set expansion up to 10 Ry in kinetic energy is included. The Brillouin zone is sampled using a special set of \vec{k} points [8 points for an assumed cell of 56 atoms for the (8,2) structure, 12 points for a corresponding of 40 atoms for (10,0) tube, and 20 points for a cell

of 24 atoms for (6,6) structure] generated in the Monkhorst-Pack scheme.¹⁰ All the systems studied have been relaxed until the components of the Hellmann-Feynman forces are smaller than 0.005 eV/Å. In the supercell approach, for the intertube distance we have used 8 Å (vacuum distance) to avoid drawbacks in terms of the interaction between the tubes. For shorter distances, we observed a distortion, implying a broken symmetry. For C nanotubes, in accordance with Blase *et al.*,¹¹ a distance of 5.5 Å is necessary to neglect the tube-tube interactions.

We have chosen to study three nanotubes, the (6,6), which has an armchair structure, the (10,0), which has a zigzag structure, and the (8,2), which has a mixed structure. All of them have similar diameters, of the order of 12 Å. The unit cell of each structure, when unfolded, can generate a graphitelike sheet. Considering the special \vec{k} points generated in the Monkhorst-Pack scheme,^{10,12} the energy per atom of the graphitelike sheets is the same for each one of the three structures described above, as it should. We obtained for the Si graphitelike sheet a total energy value of 0.79 eV/atom higher than the total energy per atom for the silicon in the diamond structure, and for the nearest-neighbor bond distance a value of 2.250 Å.

For the tubes, we also obtained the same values for the total energies per atom for all three structures considered, which is 0.83 eV/atom higher than the total energy per atom for the diamondlike structure. This is expected, since all three structures have similar diameters. Considering that the cohesive energy for the Si bulk in the diamond structure is 4.63 eV/atom, the cohesive energies for the nanotubes studied are only 82% of the bulk cohesive energy. Comparing with carbon nanotubes that have around 99% of the cohesive energy that they would have in perfect crystalline graphite,⁴ we have a clear understanding of the difficulty in producing Si tubes. Nevertheless, another important point to discuss concerning the stability of these systems is to calculate the energy cost for curving the sheet into a cylinder. For carbon atoms this value for a (10,10) nanotube is known to be only 0.05 eV/atom.⁴ For the silicon sheet, we obtain a similar number, of the order of 0.83–0.79=0.04 eV/atom to curve the sheets into cylinders. Therefore, this shows that there is a

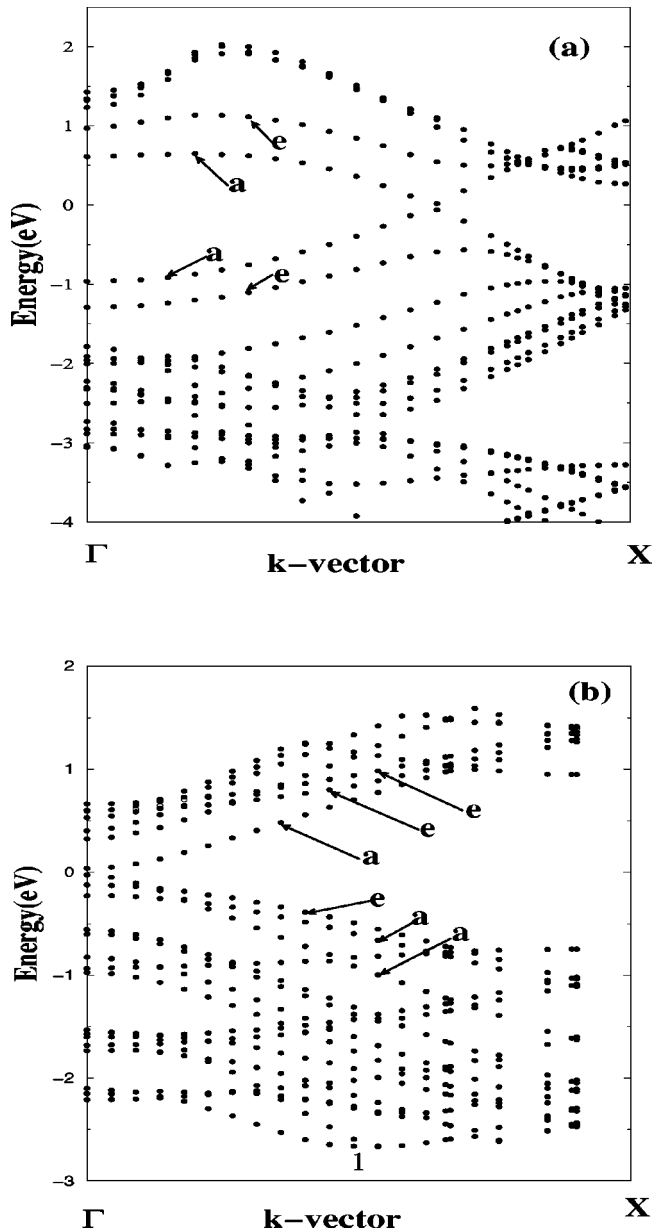


FIG. 1. The silicon band structures for (a) the armchair (6,6) tubule and (b) the zigzag (10,0) tubule. The **a** representation corresponds to a nondegenerate orbital and the **e** representation to a doubly degenerate orbital.

significant cost to produce graphitelike sheets of silicon, but once they are formed, the extra cost to produce the tubes is of the same order of the equivalent cost in carbon. The nearest-neighbor distances for the nanotubes are around 2.245 \AA , with a dispersion of 0.005 \AA , for the (6,6), (10,0), and (8,2) structures.

For carbon nanotubes, depending on their chirality, they may present metallic or semiconductor behaviors.^{4,13,14} The armchair carbon tubules are metallic and all other nanotubes present an energy gap, even though the gap decreases in inverse proportion to the tube diameter, and thus approaches zero for planar graphite. We depict our calculated band structures in Fig. 1.

The electronic band structures for different configurations for Si nanotubes are clearly very similar to the corresponding C nanotubes.² From Fig. 1(a), the metallic characteristic

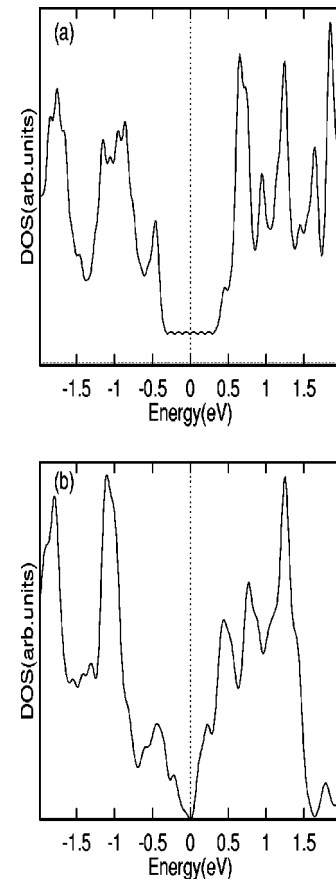


FIG. 2. The calculated density of electronic states. The density of states at the Fermi energy ($E_F=0$) is finite for (a) a metallic armchair (6,6) tube, but zero for (b) a semiconducting zigzag (10,0) tube.

of the armchair structure is evident, with the highest occupied band touching the lowest unoccupied band along the $\Gamma-X$ line in the Brillouin zone. Figure 1(b) shows the semiconducting behavior of the zigzag structure. In particular, we note that \vec{k}_F (Fermi wave vector), pinned at the point where the two bands overlap, is very similar to the value of $k_F^{tb} = 2\pi/3a$ predicted by the tight-binding model.²

Figure 2 shows the calculated density of electronic states. The density of states at the Fermi energy ($E_F=0$) is finite for a metallic armchair tube, but zero for a semiconducting zigzag tube. Scanning tunneling microscope spectroscopy on single-wall carbon nanotubes confirms all these features,¹⁵ with the normalized differential conductance $(dI/dV)/(I/V)$ being a measure of the density of states.

In this paper we have shown that the electronic properties of single-walled silicon nanotubes are very similar to the equivalent carbon nanotubes. In particular, depending on their chiralities, as happens to carbon structures, they may present metallic or semiconductor behaviors. Although the similarities in the band structures and density of states between silicon and carbon structures, and even considering the small and similar amount of energies required to curve graphitelike sheets into cylinders for both, they present a relevant discrepancy concerning the energy differences between the cohesive energies per atom for the tubes compared

with the corresponding bulks, being much bigger for silicon structures, implying the very improbable appearance of a silicon nanotube. In summary, a systematic study about the possible stability of Si nanotubes is discussed and a predic-

tion about the electronic properties of this hypothetical material is presented.

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