Tubular Structures of Siloxenes

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Using density-functional tight-binding theory we demonstrate that silicon-based tubular nanostructures in the form of siloxenes are stable and energetically viable. The structures studied here have a semiconducting gap which is independent of the chirality, but showing an increase of the gap size with increasing diameter towards that of the corresponding siloxene layer. The Si-based nanotubes are less stiff than tubes of other chemical compositions so far studied, but having Young's modulus of a magnitude similar to the bulk modulus of diamond silicon.

1. Introduction

Siloxenes, and their derivatives, have been known for a long time in chemistry [1, 2]. Siloxenes got remarkable attention in the recent years as possible active structures in the strong visible luminescence of porous silicon [3-5]. Siloxenes may be characterized as "silicon back-bone materials" where each Si atom has only three nearest-neighbour silicon atoms. The structure of a monolayer in the siloxene as it is prepared in the traditional Wöhler synthesis [1] is illustrated in Fig. 1. The structure of the "silicon back-bone", a buckled layer of sixfold silicon rings, is closely related to the starting material of the siloxene synthesis, the CaSi₂ [6]. In the Wöhler synthesis [1] the Ca ions are washed out and hydroxyl groups as well as hydrogen atoms are bound to the silicon leading to an ideal composition Si₆H₃(OH)₃ and the structure as drawn in Fig. 1 [7, 8].

The top view of the layer structure resembles much a graphene layer, see Fig. 1, though the layers are not planar as in the case of graphene but they are puckered as mentioned above. Recently, we could show that hypothetical nanotubes of the also puckered silicide layers as well as phosphorus layers corresponding to the b-P layer structure are indeed stable [9, 10]. The question arises now, whether siloxenes may also form stable tubes on the basis of the layer structures as drawn in Fig. 1.

In this paper, we consider siloxene as precursors of possible Si-based nanotubes. Using atomistic simulations within a non-orthogonal Density-Functional Tight-Binding [11-13] scheme (DFTB), we obtain the structure, energetics, electronic and mechanical properties of siloxene nanotubes. In virtue of these results we argue that the Si-based siloxene nanotubes are indeed viable.

The outline of this paper is as follows. In Section 2 we perform our DFTB calculations on the reference siloxene layers. We then describe results for a series of tubular forms based on siloxene layers, from which we obtain the equilibrium structure, the strain energy, and the electronic as well as mechanical properties of the proposed nano-



Fig. 1. Structure (side and top views) of a siloxene layer as predicted by our DFTB calculations. From the side view the OH-groups above and the hydrogens below the silicon "back-bone" layer can be seen clearly. From the top view the puckered structure of the layer is clearly visible

tubes. As a test for the stability of the tubes at elevated temperatures we present also results of molecular dynamics (MD) simulations. Finally our conclusions are summarized in Section 3.

2. Results and Discussion

Experimentally it is known [7] that siloxene consists of hexagonal puckered layers, in which the Si–Si bond distance is 2.34 Å, the Si–H bond length is 1.54 Å and the Si–O bond length is 1.60 Å. The Si–O–H bond angle is 115° [5]. The Si–Si bond distance is close to the Si–Si distance in diamond silicon. Our DFTB calculations also predict the puckered layer structure as a stable configuration (see Fig. 1), having bond distances of 2.34, 1.51 and 1.63 Å for the Si–Si, Si–H and Si–O bonds, respectively. The Si–O–H bond angle is obtained also to be 115°.

In order to study the energetic viability of the corresponding siloxene nanotubes, as well as to determine their possible structures and characterize their electronic and mechanical properties, we have performed a series of calculations in which initial-guess tubular structures have been fully relaxed with respect to atomic positions and tube cell length. Initial configurations of the nanotubes were constructed by folding 2D sheets of the corresponding siloxene layers. In labeling these tubes we adopt the convention of Ref. [14]. Depending on the rolling direction **B** in the 2D lattice $\mathbf{B} = n\mathbf{a} + m\mathbf{b}$ (\mathbf{a}, \mathbf{b} are lattice vectors of the hexagonal lattice) three classes of nanotubes can be constructed: armchair nanotubes (n, n), zig-zag nanotubes (n, 0) and "chiral" nanotubes (n, m) with $n \neq m$. We have considered both armchair nanotubes (n, n) with $n \in [6, 20]$. For each nanotube thus constructed, a set of structural relaxation

calculations were performed, each one imposing a different axial strain on the tube, with the aim of finding the atomic configuration and lattice parameter of minimum energy. Structural relaxation was performed using the conjugate gradient technique [15] in which all atoms were allowed to relax, and no constraints were imposed on the system.

Figure 2 illustrates the minimum energy structures found for siloxene nanotubes, for the (8,0) and (8,8) nanotubes, respectively. The siloxene nanotube structures can be understood in terms of those of the conventional graphitic carbon nanotubes by simply replacing the flat hexagons present in the latter by cyclohexane-like rings, just in the same way as the layered structure of the siloxene is related to that of graphene. The structures shown in Fig. 2 are representative of those found for all the other tubes considered in this work, which differ from these only in diameter and thus in the number of hexagon-like rings around the section of the tube. The results indicate the possibility of the existence of stable tubular siloxene structures. This is strongly supported by the calculated strain energy of siloxene nanotubes as a function of the tube diameter shown in Fig. 3. The strain energy is the energy difference between a tube and the corresponding reference layer structure. The calculated strain energies of the siloxene tubes are clearly smaller than those of carbon nanotubes [16], and they are also smaller than the strain energies of silicide tubes [9]. They all converge roughly as $1/D^2$ towards the value of the reference structure (strain energy zero) as the diameter D is increased, which can be easily understood from elasticity theory [17].

The discussion above suggests the stability of tubular siloxene structures at T = 0. In order to proof the stability of the tubes at elevated temperatures we performed MD



Fig. 2. Structure of (8,0) and (8,8) siloxene nanotubes. On the right a side view is shown. On the left views down the axis of the nanotubes are shown. The hydrogen atoms are pointing inward the tube, the OH-groups are bound outside of the tube



Fig. 3. Strain energies of (n,0) (open squares) and (n,n) (closed squares) siloxene nanotubes as a function of the tube diameter

simulations at 800 K. As an example, the results of such simulation for a (8,0) tube are drawn in Fig. 4. In this figure the time evolution of the outer diameter (D_{max}) , the inner diameter (D_{min}) and the shell thickness (Δ) are drawn. The corresponding temporal averages

are also shown. (They are obtained as an average over the last picosecond of the simulation after the equilibration time.) First of all, from this figure one can clearly deduce that the tube does not collapse at this temperature. At the beginning of the simulation the outer diameter inreases rapidly, whereas the inner diameter decreases simultaneously, but after about 0.5 ps the tube is relaxed and after about 1 ps more only thermal fluctuations around average values can be seen. Compared to T = 0 the diameter of the tube (D_{max}) is increased by about 10% and the shell thickness grows from a little bit less than 1 Å to about 2 Å, which indicates that the inner shell is softer than the outer shell.

The flat siloxene sheets (Fig. 1) as well as all the nanotubes considered here were determined to be semiconducting. In Fig. 5 the gap size of nanotubes has been shown as function of mean diameter. We find that the gap size grows from about 1.5 eV for



Fig. 4. Time evolution of the outer diameter D_{max} , inner diameter D_{\min} and shell thickness \varDelta for a (8,0)siloxene nanotube at T = 800 K obtained by molecular dynamics simulation (canonical ensemble). For each plotted timestep the values represent the extremal orthogonal distances of silicon back-bone atoms from the cylindrical axis. The horizontal lines mark the temporal averages over the last picosecond of simulation



Fig. 5. Gap size versus mean diameter for (n,0) (open squares) and (n,n)(closed squares) siloxene nanotubes. The gapwidth of the corresponding siloxene monolayer is indicated by the horizontal line at 1.90 eV. (Note: The gapwidth is usually underestimated within DFTB similar to LDA in general)

the smallest (n,0) nanotubes towards the value of flat siloxene sheets (1.9 eV) as the tube diameter is increased.

We next consider the mechanical properties of the siloxene nanotubes. We have calculated the Young's modulus of these nanotubes as described in earlier works [10, 16], namely by performing a series of relaxation calculations for different values of the length of the supercell in the direction of the tube axis, and thus imposing either tensile or compressive strain on the nanotube. It is then possible to calculate the second derivative of the total energy with respect to the axial strain, which enables us to calculate the Young's modulus, given by

$$Y = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \epsilon^2} \right)_{\epsilon=0}.$$
 (1)

 V_0 is the equilibrium volume, ϵ the strain and E the total energy. The definition of V_0 is not unambiguous, for a single-walled nanotube. Although several definitions have been proposed in the literature [16], most authors adopt the convention of defining V_0 as the volume of a hollow cylindrical shell of the same diameter as the nanotube and a shell thickness equal to the interlayer spacing in graphite (3.35 Å), a definition appropriate for carbon nanotubes. Adopting the same definition here can be justified for the purpose of comparing the stiffness of Si-based nanotubes with that of other nanotubes for which the Young's modulus has been evaluated using the same convention. In any case, we point out that it is the second derivative of the energy present in Eq. (1) that dictates the actual stiffness of the tube.

We have calculated the Young's modulus for the siloxene nanotubes using Eq. (1) and the volume definition outlined above. The results obtained are listed in Table 1. The siloxene nanotubes have values of the Young's modulus, which fall in the range 70–80 GPa. These values are smaller than those predicted [10] for phosphorus nanotubes, about 300 GPa, and much smaller than those of carbon and BN nanotubes [16]. The Young's moduli of the siloxene tubes are only slightly larger than those of the silicide nanotubes [9] and they are nearly equal to those of silane NTs [9], which are given also for comparison in Table 1. That means, the Young's moduli are dictated by

Table 1

Mechanical properties of siloxene (Si₆H₃(OH)₃) and silane (SiH) nanotubes as obtained from our DFTB calculations. The mean diameter \overline{D} as measured from the equilibrium structures at zero strain is also given. The Young's modulus is given in GPa as calculated from the conventional formula (Eq. (1))

(n,m)	SiH		Si ₆ H ₃ (OH) ₃	
	$\bar{D}(nm)$	Y(GPa)	\bar{D} (nm)	Y (GPa)
(6,0)	_	_	_	_
(7,0)	0.89	73.9	0.89	72.8
(8,0)	1.00	75.2	1.01	73.8
(9,0)	1.12	76.0	1.13	74.9
(10,0)	1.24	76.5	1.26	75.2
(16,0)	-	-	2.00	75.6
(20,0)	-	-	2.50	78.4
(6,6)	1.28	77.3	1.29	74.9
(7,7)	1.50	78.0	1.52	75.1
(8,8)	1.71	80.0	1.73	77.3
(9,9)	1.93	71.1	1.95	76.9
(10,10)	2.13	78.3	2.16	75.6
(16,16)	-	-	3.45	75.3
(20,20)	-	_	4.31	74.8

the stiffness of the Si–Si chemical bonds along the tube. Since in the siloxene nanotubes as well as in the silane nanotubes the Si atoms adopt an sp³ hybridization, it may be concluded that the stiffness of the tubes should be similar to the mechanical properties of crystalline Si. Indeed we find that using the same theoretical model the bulk modulus of diamond-Si is predicted to be 98 GPa, which is in very good agreement with the experimentally measured value. It should be mentioned that while this value is different from the values of Y quoted for the nanotubes, it is certainly of the same order of magnitude. The difference is partly due to the different atomic arrangements and bonding situation, and also to the fact that we have chosen V_0 in Eq. (1) so as to compare with the stiffness of other types of nanotubes, rather than with bulk silicon.

3. Conclusions

Our calculations show that stable siloxene nanotubes as an example for Si-based nanotubes should be energetically viable and therefore could exist.

All the siloxene nanotubes, proposed in this paper, have a stable semiconducting gap, independent of their chirality. The gap size increases with the tube diameter approaching the gap of the corresponding siloxene layer structure for the largest tubes considered here. As we have pointed out already for phosphorus NTs [10], the siloxene nanotubes as well as silicide and silane (SiH) tubes [9] may be promising for a use in nanoscale optoelectronic devices. Also the doping of these NTs is an interesting point to consider. Furthermore, these NTs could be of great interest for building metal–semiconductor heterojunctions with carbon NTs [18].

We have also shown that the siloxene nanotubes are less stiff than other types of nanotubes hitherto considered, including P, BN or C nanotubes. The calculated Young's

modulus is in the range that could have been expected from the mechanical properties of bulk silicon.

Regarding possible routes for synthesizing siloxene NTs, one might imagine that the variation of the reaction conditions for the siloxene synthesis from the layered silicide material could already lead to the formation of tubular siloxene structures. Furthermore, if it will be possible to synthesize silicide NTs, as we proposed in a previous paper [9], the siloxene nanotubes should be accessable from those by the traditional siloxene synthesis. The MD simulations at T = 800 K support the possibility to synthesize stable siloxene nanotubes.

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