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Tubular structures of silicon

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In this paper we demonstrate, using density-functional tight-binding theory, that certain classes of silicon-based tubular nanostructures are stable and energetically viable. Specifically, we consider silicide and SiH nanotubes. The structures adopted by these nanotubes are very similar to those of previously reported phosphorus nanotubes. As in that case, the Si-based nanotubes have a semiconducting gap, which in contrast to carbon nanotubes is largely independent of the tube diameter and chirality. We further report on the mechanical properties of the Si-based nanotubes and suggest possible routes towards their synthesis.

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There is a large interest in one-dimensional (1D) silicon structures as possible elements of nanoelectronic devices. Recently, the prototypes of carbon nanotube (CNT) and silicon nanowires heterojunctions could be realized.[1] However, there are up to now no efficient ways for synthesizing 1D Si structures. This is certainly also due to a deficiency in the understanding of structural, energetic, and electronic properties of such structures. Menon and Richter[2] propose quasi-one-dimensional Si structures, characterized by a core of bulklike fourfold-coordinated atoms surrounded by a structure related to known reconstructed surfaces with a large part of threefold-coordinated atoms. While the authors claim that such structures are typical for Si nanowires, Marsen and Sattler[3] proposed a model consisting of fullerenelike structures for Si nanowires. So far it seems to be clear that the 1D Si structures synthesized up to now (nanowires) consist of a silicon core and the surface may contain also considerable amounts of SiO_x,[1,4] i.e., these structures are not hollow, in contrast to 1D CNT's. This behavior can easily be explained by the inability of Si to form strong π bonds and in this way stabilizing threefold (sp^2) coordination, which is connected with the stability of 2D (graphene), 1D CNT's, or fullerene-like structures of carbon. The overlap of the p-π atomic valence orbitals for carbon is about 10 times larger than that for silicon at corresponding equilibrium distances, i.e., any significant π bonding contribution in Si structures can be excluded. Therefore, the report[5] about the hypothetical existence of Si nanotubes seems to be doubtful.

However, it should be mentioned that there are indeed layered silicon systems among the inorganic crystalline modifications. Alkaline-earth-metal silicides consist of flat silicon layers separated by the alkaline-earth-metal ions.[6] Each silicon atom is threefold coordinated by silicon atoms. Formally, the silicon atoms are negatively charged in these silicides—e.g., $\mathrm{CaSi_2}$-Ca^{2+}, Si^-. Thus, silicon becomes isoelectronic to phosphorus in the silicides, and it is well known that phosphorus forms a layer structure, known as black phosphorus (b-P).[7] As in b-P the silicon layers in the silicides are not ideally planar—as in graphene, but become puckered, as shown in Fig. 1, left panel. On the other hand, the top view of the layer structure greatly resembles a graphene layer. Recently, we could show that hypothetical nanotubes of phosphorus corresponding to the b-P layer structure are indeed stable.[8] At this point, questions arise whether silicon may also form stable tubes on the basis of the silicide layer structure corresponding to phosphorus. Furthermore, silicides may also be used for the synthesis of polymeric SiH, the structure of which unfortunately up to now is not yet well characterized. But one can easily imagine that SiH may form a puckered layer as illustrated in Fig. 1, right panel, and therefore, being also a candidate for Si-based nanotube structures.

In this paper, we consider silicides and SiH as precursors of possible Si-based nanotubes. Using atomistic simulations within a nonorthogonal density-functional tight-binding[9–11] scheme (DFTB), we obtain the structure, energetics, electronic and mechanical properties of silicide and SiH nanotubes. In virtue of these results we argue that the Si-based nanotubes are indeed viable.

Experimentally it is known[6] that, e.g., $\mathrm{CaSi_2}$ consists of

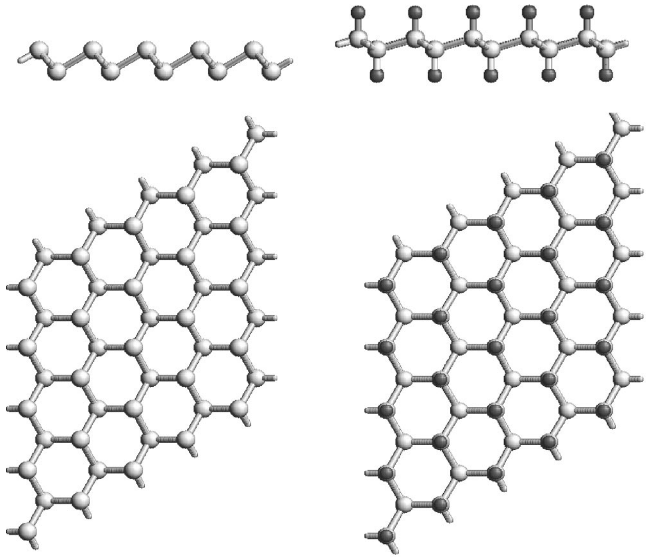

FIG. 1. The structure (side view, upper figure; top view, below) of a silicide (left) and SiH layer (right) as predicted by our DFTB calculations. From the top view the puckered structure of the layer is clearly visible.

hexagonal puckered layers, in which the Si-Si bond distance is 2.41 Å, and has a Si-Si-Si bond angle of 104.8°. The Si-Si bond distance and the bond angles are close to the P-P distance and similar to the P-P-P angles in the *b*-P,[7] confirming the similarity between these two systems. The puckered Si layers are separated by planar layers of Ca with a Ca-Si distance of 3.82 Å. Since we are mainly interested in the layer properties we assumed a complete ionic model concerning the Ca-Si interaction and considered in our calculation the Si layer only with one aditional electron per Si atom (corresponding to Ca^{2+}, Si^{-}). The positive countercharge was treated as a homogeneously distributed background charge. Our DFTB calculations also predict within this model the puckered layer structure, shown in Fig. 1, left panel, as a stable configuration, having a bond distance of 2.49 Å, and all bond angles having a value of 96°, in reasonably good agreement with the experimental values for CaSi_2. We find also a puckered layer structure as a stable configuration for SiH; see Fig. 1, right panel. The Si-Si bond distances are calculated as 2.34 Å and the Si-H bond length is 1.51 Å, which are close to the Si-Si and Si-H bond lengths in disilane ($\mathrm{Si}_2\mathrm{H}_6$).[12]

In order to study the energetic viability of the corresponding Si^{-} and SiH nanotubes, as well as to determine their possible structures and to 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 a 2D graphenelike sheet of a Si layer with a Si-Si bond distance of 2.49 Å, i.e., that obtained for the silicide sheet. Our starting structures were obtained from flat sheets rather than the buckled structure of Fig. 1 so as to not bias the structures of the nanotubes. However, the high symmetry of the hexagonal structures was broken by small random displacements of the atoms in order to facilitate the convergence of the calculations. In labeling these tubes we adopt the convention of Ref. 13. We have considered both armchair nanotubes (n,n) with $n \in [6,10]$, and zigzag nanotubes, $(n,0)$, with $n \in [6,10]$. 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 gradients technique[14] in which all atoms were allowed to relax, and no constraints were imposed on the system.

Figures 2 and 3 illustrate the minimum energy structures found for silicide (8,0) and (8,8) nanotubes, respectively. These fascinating 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 cyclohexanelike rings, just in the same way as the layered structure of the silicides is related to that of graphene. The two structures shown in Figs. 2 and 3 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 cyclohexane rings around the section of the tube. It should be mentioned that the structure of these silicide tubes is nearly identical to those of corresponding phosphorus nanotubes (NT's) that we have described in a previous paper.[8] Of course, the P NT's are neutral, whereas the silicide tubes are charged and the counterions have not yet been considered specifically. Nevertheless, the results indicate the possibility of the existence of stable tubular silicon structures in form of silicides. This is strongly supported by the calculated *strain energy* of silicide nanotubes as a function of the tube diameter, shown in Fig. 4. The strain energy is the energy difference between a tube and a reference structure, which in the case of Si we take to be the silicide layer of Fig. 1, while for

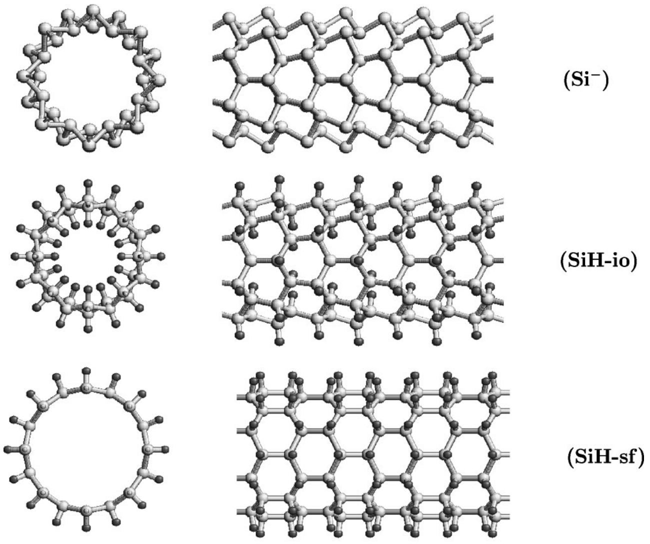

FIG. 2. Structure of the (8,0) silicide, SiH-io, and SiH-sf nanotubes. On the right, side views are shown. On the left, views down the axis of the nanotubes are shown.

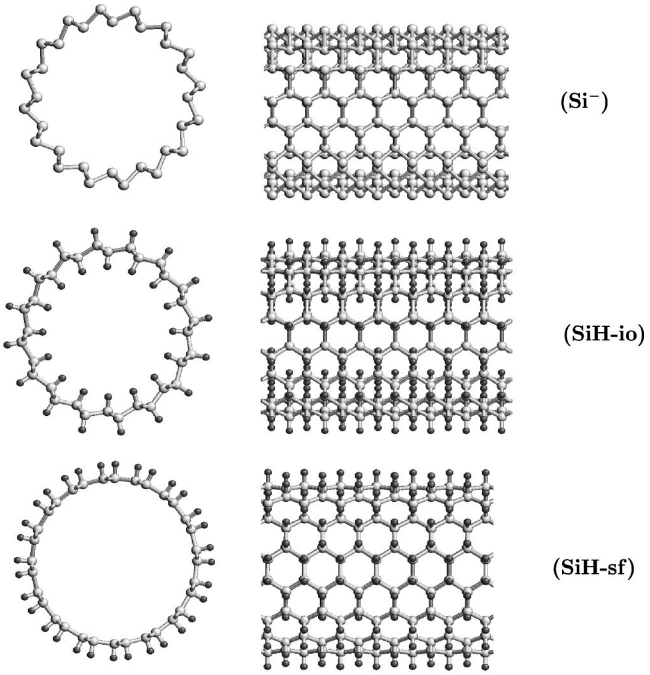

FIG. 3. Structure of the (8,8) silicide, SiH-io, and SiH-sf nanotubes.

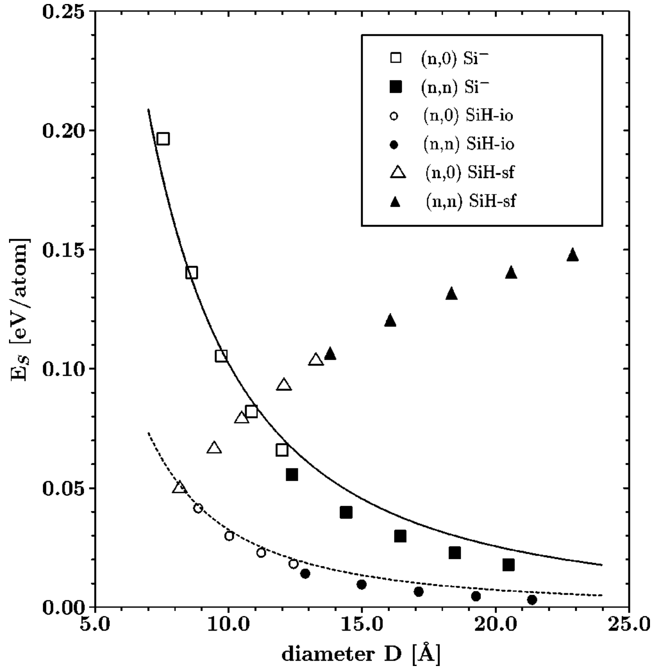

FIG. 4. Strain energies of (n,n) and $(n,0)$ silicide (Si^-), SiH-io and SiH-sf nanotubes as a function of the tube diameter. Note: The energies of SiH-io and SiH-sf tubes are both calculated with respect to the SiH layer structure as shown in Fig. 1, i.e., for the SiH-sf tubes the data do not really correspond to a strain energy, but the presentation shown allows an energetic comparison for all tubes on the same scale.

carbon nanotubes it is a flat graphene sheet.[15] Note, that for a given diameter, the strain energy of the silicide nanotubes is only slightly larger than that of the graphitic nanotubes,[15] but smaller than that of the P NT's.[8] 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 understood easily from elasticity theory.[16]

For SiH tubes we considered two limiting cases for $(n,0)$ and (n,n) tubes. Either all hydrogen atoms are bound outside the surface of the tube (SiH-sf) or alternating inside/outside (SiH-io) as it is illustrated in Figs. 2 and 3 for $(n,0)$ and (n,n) tubes, respectively. Surprisingly, it turned out that for small diameters the SiH-sf tubes are almost isoenergetic with the SiH-io tubes. But compared to the SiH-io tubes, the SiH-sf tubes show opposite strain energy behavior than expected,[16] becoming less stable with increasing diameter. The behavior of the SiH-sf tubes can be understood quite easily. With increasing diameter of the tube and simultaneously decreasing curvature the Si-Si-H bond angle is more and more forced towards 90°, whereas in the SiH-io tubes the ideal tetrahedral angle of 109.5° for fourfold-coordinated silicon can be achieved better and better with increasing diameter; see Fig. 4. A flat 2D SiH layer with all hydrogens bound on one side would not be stable at all, but it could bend spontaneously and favor the formation of SiH-sf nanotubes with small diameters. From Fig. 4 one can clearly see that the SiH-io and small-diameter SiH-sf tubes have the lowest strain energies of all nanotubes studied up to now.

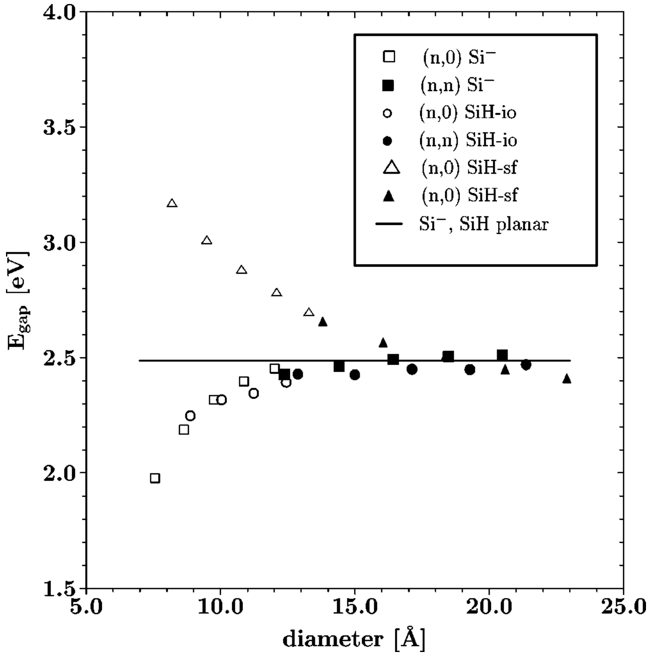

FIG. 5. Gap-size versus mean diameter for $(n,0)$ and (n,n) silicide (Si^-), SiH-sf, and SiH-io, nanotubes. The planar structures are symbolized by a single line due to nearly equal gap widths of 2.49 eV and 2.50 eV for planar Si^- and SiH, respectively.

The flat silicide and the SiH sheets as well as all the nanotubes considered here were found to be semiconducting. In our calculations the band gap in the Si^- and SiH sheet was found to be 2.49 eV and 2.50 eV, respectively. Such gap size agrees quite nicely with that obtained by other calculations[19] (2.48 eV) and experimentally[20] (2.5 eV) for the layered SiH.

In Fig. 5 have been shown the gap size of nanotubes as function of mean diameter. For silicide and SiH-io NT's we find that gap size rapidly grows towards the value of flat silicide and SiH sheets as the tube diameter is increased. For SiH-sf NT's this behavior is opposite: the gap sizes shrink down to value of the flat sheet. The discussed behavior is clearly in contrast to carbon NT's, where the band gap is strongly varying with the diameter and also with the chirality of the tubes. But a similar result was already obtained for the phosphorus nanotubes.[8]

Additionally, we studied the mechanical properties of the silicide and SiH nanotubes. We have calculated the Young's modulus of these tubes as described in earlier work.[8,15] We show that Si-based nanotubes are less stiff than other types of nanotubes hitherto considered, such as P, BN, or C nanotubes, but that their Young's modulus is in the range that could have been expected from the mechanical properties of bulk silicon. The bulk modulus of diamond-Si is predicted to be 98 GPa within the same theoretical model, compare Table I.

Summarizing, our calculations show that stable Si-based nanotubes are energetically highly favorized structures and therefore could exist. We proposed to avoid the problem of dangling bonds for threefold-coordinated silicon in tubular structures by formally charging the silicon (silicide tubes) or by saturation with hydrogen (SiH tubes).

TABLE I. Mechanical properties of silicide and 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.

	Si$^-$		SiH-io		SiH-sf	
(n,m)	$\overline{D}$ (nm)	Y (GPa)	$\overline{D}$ (nm)	Y (GPa)	$\overline{D}$	Y (GPa)
(6,0)	0.75	57.3	–	–	0.82	55.3
(7,0)	0.86	61.1	0.89	73.9	0.95	56.0
(8,0)	0.97	63.4	1.00	75.2	1.08	56.1
(9,0)	1.08	68.1	1.12	76.0	1.21	57.0
(10,0)	1.20	65.4	1.24	76.5	1.33	57.0
(6,6)	1.24	66.9	1.28	77.3	1.38	68.7
(7,7)	1.44	71.4	1.50	78.0	1.60	69.2
(8,8)	1.64	66.1	1.71	80.0	1.84	68.7
(9,9)	1.85	69.4	1.93	71.1	2.06	68.1
(10,10)	2.05	68.5	2.13	78.3	2.29	67.6

All the silicide and SiH nanotubes proposed in this paper have a stable semiconducting gap, independent of their chirality, which converges rapidly with increasing diameter to that of the 2D layer. As we have pointed out already for phosphorus NT's,[8] also silicide and SiH tubes may be promising for a use as nanoscale optoelectronic devices, and the doping of the Si-based NT's is an interesting point to consider. Furthermore, these NT's could be of great interest for building metal-semiconductor heterojunctions with carbon NT's.[1]

Based on stability considerations compared to CNT's, we argue that synthesis of silicide as well as SiH NT's could be achieved. Concerning the silicides there exist, despite the layered structures, already a large variety of cluster structures,[17] i.e., the 1D tubular structure may be viewed as the missing link between the 2D silicides and the silicide cluster compounds. Varying the reaction conditions for silicide synthesis could therefore be a promising way to fabricate silicide nanotubes. For SiH tubes the layered silicide structures are probably also appropriate starting materials. The synthesis of SiH systems from silicides has been known for more than 30 years;[18] however, up to now it has not been well understood and studied in detail. Therefore, in this way tubular structures may even be formed. One could also think about synthesis by glow discharge processes of monosilane.

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