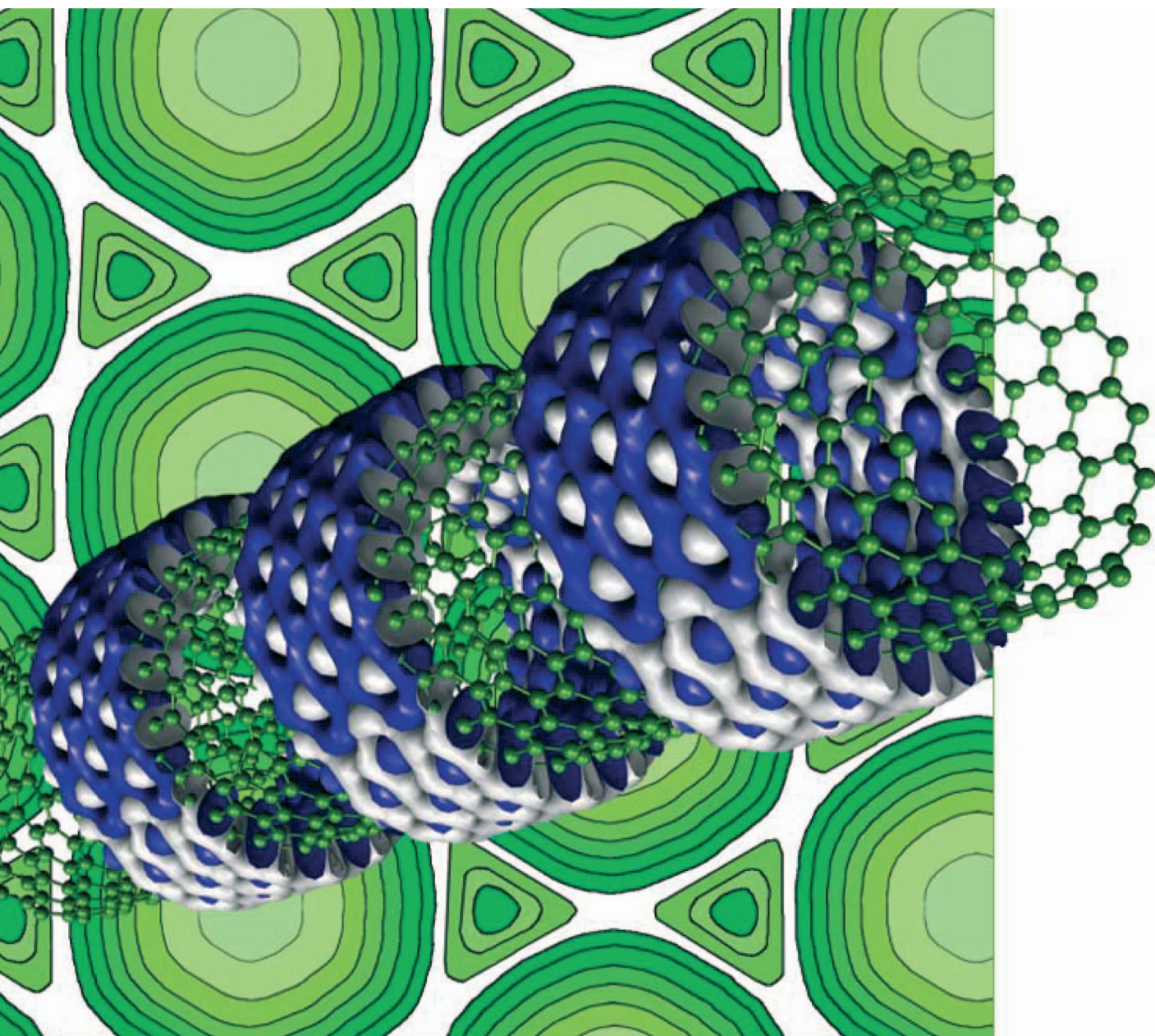


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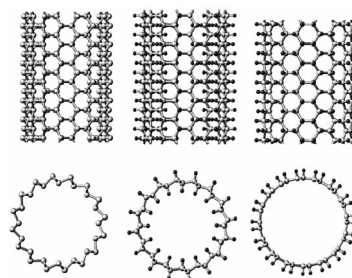
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Silicon Nanotubes

New Si units! Only very recently has it been shown that it is possible to prepare nanotubes from silicon. The impact of such materials could be enormous in, amongst other fields, the electronics industry. Initial studies have shown that there is some complexity in understanding these materials and some diversity from their carbon-based cousins (the image shows various possible nanotubes, viewed parallel and perpendicular to the plane of the page).



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Silicon Nanotubes

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- nanowires
- silicon

Silicon has been widely recognized as the most important material of the 20th century. This is largely due to its role as the fundamental component in integrated circuits and consequently in the microelectronic revolution. From a chemical point of view, similar to the other group IV elements, silicon easily forms four covalent σ bonds in tetragonal coordination (sp^3 hybridization) and typically crystallizes in a diamond-like structure. Unlike the case of carbon, which easily forms strong π bonds through sp^2 hybridization (spanning an enormous variety of organic molecules and carbon materials, for example, graphite, fullerenes, nanotubes), the π bond in silicon compounds is rather weak ($\approx 25 \text{ kcal mol}^{-1}$ versus $\approx 60 \text{ kcal mol}^{-1}$ in carbon) and reactive, so that only a few stable molecules with a Si=Si double bond (π -bonding) are known. Such behavior, in turn, destabilizes the trigonal planar coordination, which promotes the crystallization of carbon into two-dimensional planar, tubular,^[1] and cage-like structures.

Substantial efforts have focused on investigating nano-scale forms of silicon, both for the purpose of further miniaturizing the current microelectronic devices and in the hope of unveiling new properties that often arise at the nano-scale,^[2] including the goal of integrating electronics and photonics on the same Si chip.^[3] Both aims were attained to a great extent by various groups, leading to silicon nanowires^[4] as well as silicon nanoclusters.^[5] The latter are particularly interesting because of their unexpected luminescence properties (while bulk silicon is a poor light emitter, because of its indirect bandgap).^[3,5]

The possibility of the existence of tubular silicon nanostructures, that is, silicon nanotubes^[1] (SiNTs), had been

previously discussed theoretically by several authors, based on density functional theory (DFT),^[6–9] Hartree–Fock,^[10] Møller–Plesset electron correlation (MP2),^[9] and semi-empirical^[10] quantum chemical calculations, as well as molecular dynamics simulations.^[9] As outlined above, this type of aggregation is particularly surprising for silicon, since π bonding (and the associated planar sp^2 -type coordination) is usually necessary to form stable two-dimensional structures (like graphene sheets), tubular structures, or cage (fullerene-like) structures. In fact, with respect to one-dimensional nanostructures, sp^3 hybridization favors the formation of Si nanowires^[4] rather than nanotubes. The theoretical models included tubular structures built of hexagons of Si in sp^2 hybridization (benzenoid structure, Figure 1 A)^[6] or sp^3 hybridization (hydrogen-terminated Si–H or anionic Si[–] (silicide) structures, Figure 1 B).^[7] More recently, a quite different model based on tetragons of sp^3 -hybridized silicon atoms has been proposed (Figure 1 C).^[9] This model is particularly intriguing since the fragments of this structure, ladder-type oligo(cyclotetrasilane)s (Scheme 1), are known as stable molecules (in contrast to fragments of sp^2 SiNTs, for example, the hypothetical hexasilabenzene).^[11]

DFT calculations have also been used to predict the mechanical and electronic properties of SiNTs. Seifert et al. calculated a Young's modulus of 70–80 GPa for H-terminated sp^3 SiNTs (over an order of magnitude lower than for carbon nanotubes), which were predicted to behave as semiconductors with a bandgap of 2–3 eV.^[7] By calculating sp^2 SiNTs, Fagan et al. concluded that the bandgap depends on the chirality, with armchair tubes being metallic, while the chiral tubes are low-bandgap semiconductors.^[6] Also, a zero bandgap was suggested for sp^3 tetragonal SiNTs by Bai et al.^[9]

Only recently, however, has the synthesis of SiNTs been demonstrated by various groups, each using a different growth process. Yang et al.^[12,13] first reported the synthesis by chemical vapor deposition and experimental observation by transmission electron microscopy (TEM) of large-diameter SiNTs ($\approx 50 \text{ nm}$). The tubes were grown on alumina nanochannel arrays using gold particles as catalysts. Lee and co-workers^[14] later reported the growth of SiNTs by molecu-

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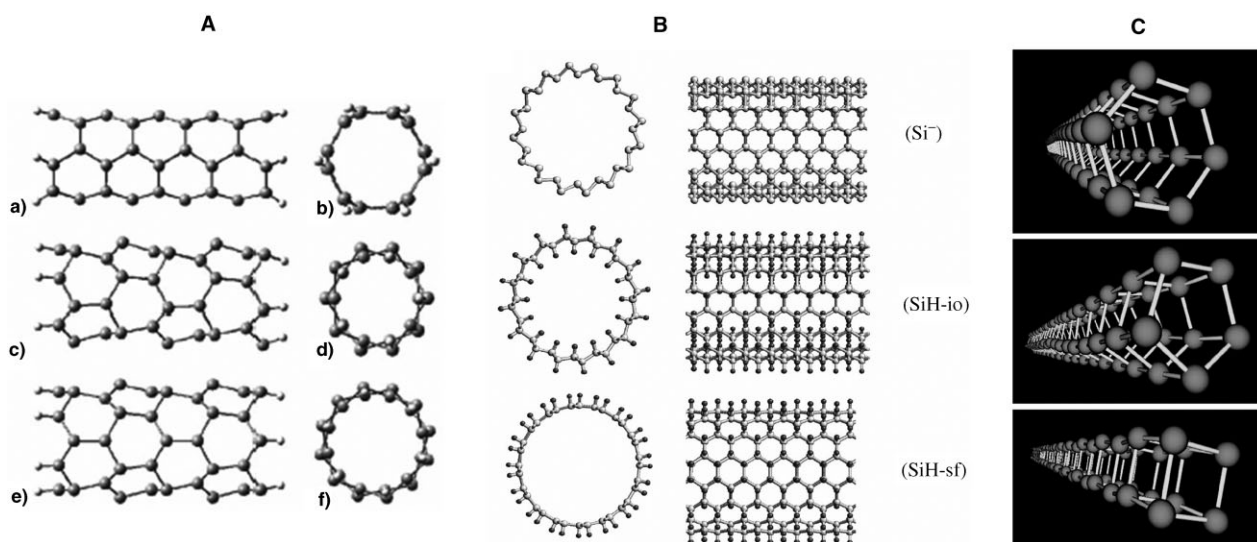
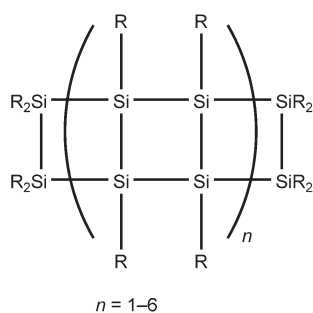


Figure 1. Calculated structures: A) An sp^2 SiNT. Armchair (3,3) nanotube ($Si_{54}H_{12}$), its axis along the plane of the page (a) and perpendicular to the page (b); zigzag (5,0) nanotube ($Si_{50}H_{10}$), its axis along the plane of the page (c) and perpendicular to the page (d); zigzag (6,0) nanotube ($Si_{60}H_{10}$), its axis along the plane of the page (e) and perpendicular to the page (f). Reprinted with permission.^[6] B) sp^3 SiNTs in their hydrogen-terminated (SiH-io, with hydrogen atoms in alternating inside/outside positions, and SiH-sf, with all hydrogen atoms being on the outer surface) and silicide (Si^-) structural forms.^[7] C) sp^3 tetragonal SiNTs of different diameters. Reprinted with permission.^[9]



Scheme 1. The structure of oligo(cyclotetrasilane)s.

lar beam epitaxy on porous alumina, without using catalysts. The observed tubular structures were covered with a thick layer of silicon oxide (≈ 10 nm). These SiNTs exhibit a photoluminescence peak at a wavelength of 600 nm, which was ascribed to quantum confinement effects. Arguably, however, in these first observations, the Si atoms aggregated inside the templates in a disordered fashion with no sign of crystallinity.

More recently, Tang et al.^[15] demonstrated the self-organized growth of smaller-diameter (≈ 13 nm) SiNTs via hydrothermal synthesis, using silicon monoxide (SiO) as the starting material (without the use of catalysts).^[16] Based on a high-resolution TEM micrograph of the obtained nanotubes, the authors suggested a multiwalled structure with an interlayer spacing of 0.31 nm, covered with a thick oxide layer that can be removed by HF treatment (Figure 2).^[15,16] The interlayer spacing is intriguing, since a larger spacing of ≈ 0.4 nm is expected based on the van der Waals radius of Si (0.21 nm). Alternatively, the 0.31-nm spacing could simply represent the separation between the (111) planes in crystalline silicon. Finally, by measuring the periodicity of

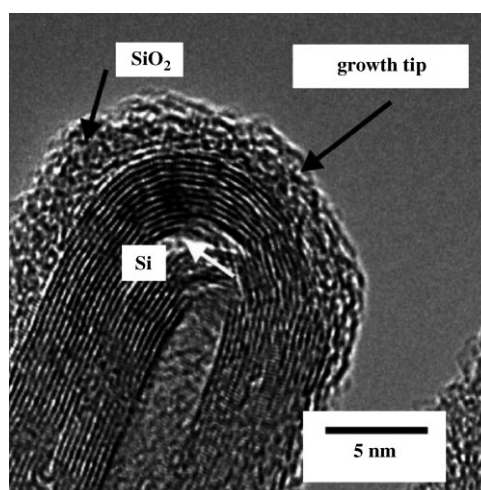


Figure 2. TEM image of a silicon nanotube grown from silicon monoxide. Reprinted with permission.^[16]

the SiNTs using the scale bar of the TEM micrographs reported in the two reports,^[15,16] we obtain interlayer spacings of 0.22 and 0.29 nm, respectively, which are quite different from the claimed spacing of 0.31 nm. Thus, we are of the opinion that the data presented by Tang et al.^[15,16] does not allow us to clearly discern the claimed multiwalled structure from the periodicity of an sp^3 -type Si nanocrystal (which has a hollow “tubelike” structure).

Finally, De Crescenzi and co-workers most recently reported the synthesis and experimental observation of thin (presumably single-walled) SiNTs.^[17,18] High-resolution TEM, localized electron energy loss spectroscopy (EELS), and scanning tunneling microscopy (STM) were employed to discern Si nanotubes, which formed in $\approx 10\%$ yield

among various other products (mostly silicon oxide nanoparticles) by way of an arc-discharge gas-phase condensation synthesis. Some of these tubes were as small as 2 nm in diameter, the smallest SiNTs reported so far. Due to strong attractive Van der Waals interactions, these Si nanotubes are observed to be radially compressed when adsorbed on graphite, similar to the case of carbon nanotubes.^[19,20] From atomically resolved STM images (which show a well-ordered Si surface), the authors identified SiNTs of different chirality and measured their local density of states (LDOS) by scanning tunneling spectroscopy (STS). The combination of STM and STS allowed the authors to correlate the tubes' chirality with their electronic structure, thus suggesting that these SiNTs exhibit a metallic behavior for nonzero chiral angles, that is, for those tubes that are not of the armchair configuration (Figure 3).^[17] This result is somewhat surprising since an opposite trend was observed in carbon nanotubes (i.e., armchair carbon nanotubes are metallic, and

most of the chiral tubes are semiconducting). We also emphasize that a zero bandgap (metallic behavior) has been predicted by DFT calculations for armchair sp^2 -hybridized SiNTs, while the chiral tubes were concluded to be semiconducting.^[6]

One of the most intriguing features of the SiNTs reported by De Crescenzi et al. is their high stability towards oxidation. Both their EELS and STM data indicate that the tubes are not (significantly) oxidized after exposure to air. Such stability would be most unexpected for π -bonded sp^2 SiNTs and, together with the EELS Si $L_{2,3}$ peak position (101.5 eV), suggest an sp^3 -hybridized structure. A similar stability of Si nanowires was explained in terms of hydrogen termination of the surface (which is invisible to STM imaging).^[4b] However, the possibility of hydrogen termination of the SiNTs reported by De Crescenzi et al. is unlikely since there was no evident source of hydrogen.^[17]

In conclusion, after many years of speculation, the experimental synthesis of SiNTs has now been demonstrated by several groups. These findings are very likely to impact the future development of the chemistry of silicon. They may also lead to novel nanoelectronic, nanophotonic, and nanosensor devices. However, of the four experimental reports on Si nanotubes published so far, none of them describes a realistic model for the growth process and overall properties of these novel one-dimensional systems, and there is limited agreement with previous theoretical predictions. The structure of SiNTs is still an open question of fundamental physical and chemical importance, which clearly requires concerted efforts between theoreticians and experimentalists. We expect that it will not be long before such studies, with new reported SiNTs, enrich our understanding of how matter is assembled into stable forms.

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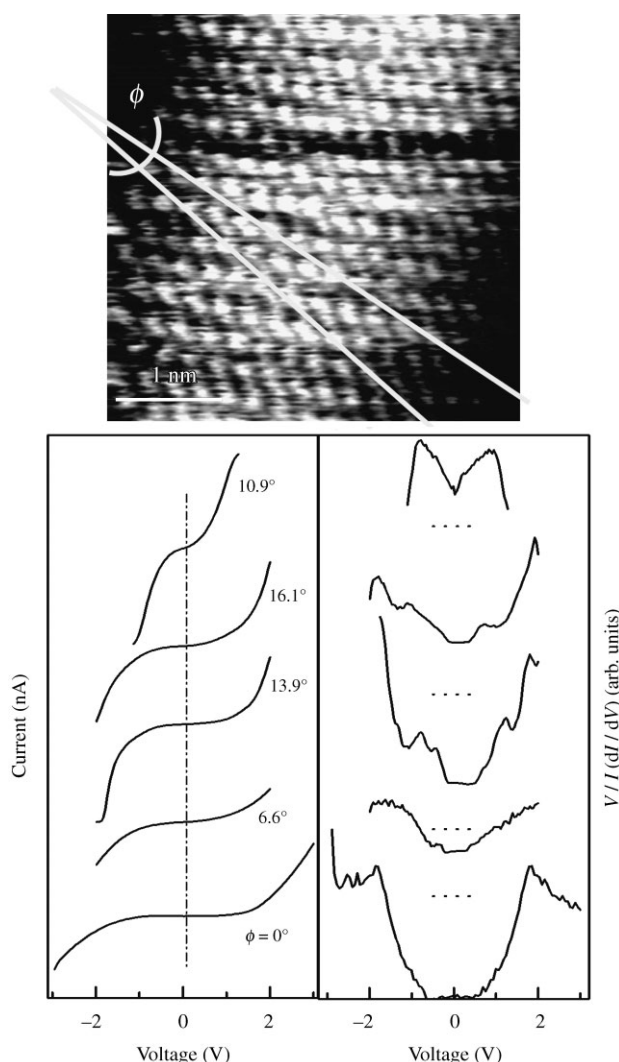


Figure 3. Upper panel: Atomically resolved STM image ($4 \times 4 \text{ nm}^2$) of part of the lateral surface of a silicon nanotube. Lower panel: left) I - V curves obtained by STS on six individual silicon nanotubes characterized by different chiralities (angle ϕ); right) normalized conductances $V/I(dI/dV)$ of the I - V curves.^[17] Courtesy of M. De Crescenzi.

[1] Nanotubes are peculiar one-dimensional tubular nanostructures, in which one (single-walled) or more (multiwalled) sheets of a certain element or compound are rolled into a tube. Because of their size and shape, they require specific directional bonds to be stable. Carbon nanotubes were reported for the first time by S. Iijima, *Nature* **1991**, 354, 56.

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