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Self-Assembled Silicon Nanotubes under Supercritically Hydrothermal Conditions

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Self-assembled silicon nanotubes with one-dimensional structure have been synthesized from silicon monoxide powder under supercritically hydrothermal conditions with a temperature of 470 °C and a pressure of 6.8 MPa. The silicon nanotubes were identified by transmission electron microscopy and high-resolution transmission electron microscopy. The results show that the silicon nanotubes (SiNT) have closed caps. The structures of the silicon nanotubes are hollow inner pore, crystalline silicon wall layers with a 0.31 nm interplanar spacing and 2–3 nm amorphous silica outer layers. Pure crystalline silicon nanotubes survive after etching the silicon nanotubes with 5% HF acid for enough time to imply that the self-assembled silicon nanotubes are stable. A possible theoretical reason for the growth of SiNTs from SiO under supercritically hydrothermal conditions was also proposed.

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Recently, there has been particular interest in one-dimensional nanomaterials, such as silicon nanowires (SiNWs) [1–4] and carbon nanotubes (CNTs) [5]. It is because of their novel properties and potential applications. CNTs have attracted much attention in the fields of nanoscience and nanotechnology due to their unique structural and electronic properties since the discovery in 1991 [5]. SiNTs would have better compatibility with the present established Si technology and may open up new and exciting possibilities for making different kinds of nanosized heterostructures by filling the inside (hollow) space with one type of nanomaterial and/or by decorating the outside surfaces of the nanotubes with another type of nanomaterial [6]. It should be noted that carbon has sp^2 hybridization, whereas silicon has sp^3 hybridization. Therefore, synthesis of hollow one-dimensional SiNTs is difficult owing to sp^3 hybridization in silicon, other than sp^2 hybridization in graphite. However, the existence of SiNTs has been calculated theoretically. Zhang *et al.* [7] studied hypothetical SiNTs using the semiempirical molecular orbital PM3 method and referred that SiNTs with puckered surface structures could be formed in principle under appropriate conditions. Ivanovskaya *et al.* [8] investigated hypothetical SiNTs containing regular chains of metallocarbohedrenes using a one-dimensional tight-binding model within Hückel approximation. Hypothetical SiNTs were also studied using density functional theory calculation based on B3LYP/6-31G(d) [9]. Some stable silicon tubular structures were also found to exhibit semiconducting properties independent of tube diameter and chirality [10]. Kumar *et al.* [11] showed that stable hydrogenated Si fullerenes with empty centers by using an *ab initio* ultrasoft pseudopotential plane wave and generalized gradient approximation for the exchange-correlation energy. Recently, Jeong *et al.* [12] fabricated SiNTs on the alumina template in the molecular beam epitaxy chamber. Sha *et al.* [13] synthesized SiNTs by the chemical vapor deposition process using a nanochannel Al_2O_3 substrate. However, the formation of SiNTs is disordered aggregation of silicon atoms in the inner wall of templates which cannot form good crystal structure. Researchers around the world are attempting to prepare self-assembled SiNTs which are real SiNTs.

Hydrothermal synthesis of CNTs [14,15] demonstrates the potential of the hydrothermal method for preparing one-dimensional nanomaterials. Hydrothermal synthesis of materials has many advantages over other methods; i.e., it is environmentally benign, inexpensive, and allows for reduction of free energies for various equilibria [16]. Supercritical water offers a different chemistry under pressure, sufficient density to dissolve materials, a higher diffusivity than in a liquid state, a low viscosity facilitating mass transport, and high compressibility allowing for easy changes in density and dissolving power [17]. Here we report that self-assembled SiNTs synthesized by the supercrictically hydrothermal process and pure crystalline SiNTs can survive after HF etching self-assembled SiNTs for enough time. The formation of initial SiNTs and the growth process are discussed in detail to explain the possible growth mechanism of SiNTs.

The starting materials are silicon monoxide and deionized water. 2.5 g of SiO powder (purity: 99.99%, particle size: ~73 μm, density: 2.1 g/cm^3) was mixed with about 47.5 ml deionized water. Then the mixture was put into a reaction kettle with a volume of 1000 ml. The reaction kettle was heated to 470 °C , 6.8 MPa , 200 r/min (the rotating speed for the stirrer equipped in the kettle after it was sealed), and the temperature and pressure were maintained for 1 h. Subsequently, the reaction kettle was cooled naturally. A light yellow aqueous solution with some suspension was collected after the experiment. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) samples were prepared by putting several drops of solution with suspension onto a standard copper grid with a porous carbon film. TEM and HRTEM observations were performed using a JEOL JEM 2010 transmission electron microscope with 1.9 Å point-to-point resolution operating with a 200 kV

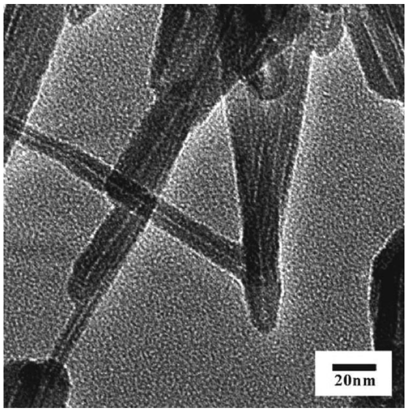

FIG. 1. Typical TEM image showing the general morphology of self-assembled SiNTs.

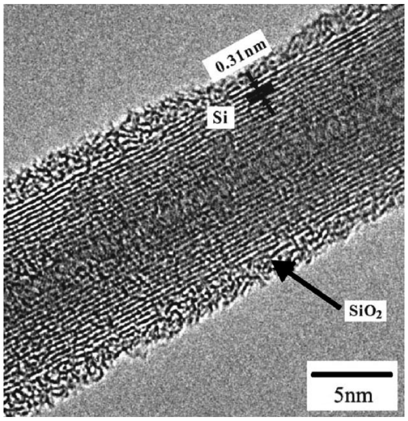

FIG. 2. HRTEM image of tubular body showing {111} lattice fringes of a single SiNT with an amorphous SiO_2 outer layer surrounding Si crystal.

accelerating voltage with a GATAN digital photography system. The samples were etched with HF acid (concentration: 5%) for 30 min and the HRTEM observation was performed using a JEOL JEM 3010 transmission electron microscope with a 1.7 Å point-to-point resolution operating with a 300 kV accelerating voltage.

The TEM image shown in Fig. 1 displays the general morphology of self-assembled SiNTs. The outer diameter of the SiNTs is about 15 nm and the diameter of the inner pore is smaller than 5 nm in average. It is somewhat like CNT. However, bulk quantities of metal catalyst particles were observed at the tips of CNTs. Metal catalysts are necessary to produce CNTs by supercritically hydrothermal conditions [18,19]. Here we emphasize that no catalysts are observed at the tips of the SiNTs. It is well known that one-dimensional nanomaterials without catalysts can take great advantage of measuring their real properties of nanomaterials. Therefore, the real properties of SiNTs can possibly be attained in the future.

Figs. 2 and 3 are the HRTEM images of typical self-assembled SiNTs. The nanotube is imaged to have a nearly parallel dark line and the interplanar spacing of crystals is 0.31 nm, according to the HRTEM measurement and following a calculation by the software of Digital Micrograph (Gatan Inc., Pleasanton, CA) applied in the HRTEM, matching well with the {111} plane of silicon. The HRTEM images show {111} lattice image of the Si tubular structure along the tubular axes. The surface is rough and coated by an amorphous silica layer. The inner and the outer diameters of a typical nanotube are 3.5 nm and 18 nm, respectively, (Fig. 3). Some defects in the SiNTs can be clearly seen. The structures of the SiNTs are hollow inner pore, crystalline silicon wall layers, and 2–3 nm amorphous silica outer layers.

It should be mentioned here that the outer diameter of the SiNTs is smaller than those of so-called SiNTs prepared by the templates method which are about 100 nm in diameter [12,13]. The smallest SiNT observed in our experiment is around 8 nm, consisting of less than 2 nm in the diameter of the inner pore. Obviously, the research of the smaller SiNTs is an interesting topic, like that of the smallest CNTs [20]. SiNTs terminate with the closed cap, as confirmed from the TEM and HRTEM observations (Figs. 1 and 3). The tips in the two sides of the SiNTs are both close, owing to the tips appearing in random. In addition, some defects (pointed out by the white arrow in Fig. 3) in the closed cap of the SiNTs are more than that of the tubular body. The defects are low energy states, so they may play an important role in forming the semicircular cap and causing the shift of closed cap from the growth axis of the SiNTs.

It would have been interesting to remove the silicon oxide with HF to demonstrate what the material survives. Therefore, the self-assembled SiNTs are treated by 5% HF acid etching for 30 min and the corresponding HRTEM images are shown in Fig. 4. Amorphous silica outer layers are removed and pure crystalline SiNTs can survive; this implies that the self-assembled SiNTs are stable.

A hypothetical SiNT Si-H self-assembled growth model is suggested by us according to the analysis on the HRTEM micrographs and theory research results. The saturation of

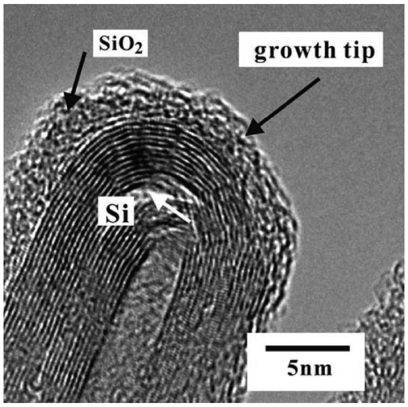

FIG. 3. HRTEM image showing the structure at the tip of SiNTs with a closed cap. Defect is existing in the closed cap pointed out by the white arrow.

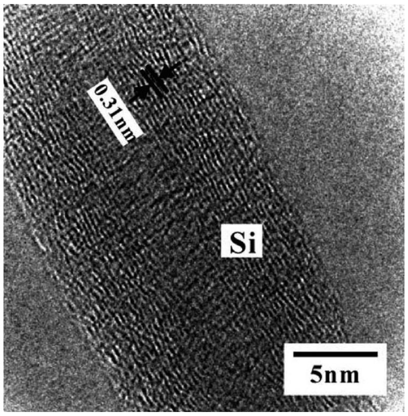

FIG. 4. HRTEM images of SiNTs after HF etching (concentration: 5%) for 30 min showing that the self-assembled SiNTs are stable.

the dangling bonds with hydrogen at the ends of a SiNT was found to crucial for the silicon tube to maintain a metastable structure, without which the structure first deforms and eventually collapses to form an irregularly shaped nanowire with mostly sp^3 hybridized Si atoms. Dangling bondings of Si were also considered important by the research of hypothetical SiNTs using a density functional theory calculation based on B3LYP/6-31G(d). H_2O vapor is ionized into H^+ and OH^- under supercritically hydrothermal conditions [21]. Therefore, the dangling bondings at the edge of SiNTs can be saturated by H^+ playing an important role during the formation and growth of SiNTs.

The SiNT Si-H self-assembled growth model is shown in Fig. 5. The hydrogen atoms are used to stabilize the structure as well as to simulate the effect of a longer tube. The cohesive energies per atom for SiNTs are higher than that for the bulk Si in the diamond structure, implying the difficulty in producing SiNTs or graphitelike sheets. However, the elastic energy per atom to curve the sheet into a tube for silicon atoms is very low when graphitelike sheets of silicon are formed according to the research of hypothetical SiNTs, based on the Tersoff potential. Therefore, the probability of the existence of SiNTs increases when SiNTs are composed of both sp^2 and sp^3 bonds and the ratio of sp^3 to sp^2 is high. SiNTs similar to multiwalled structures can be formed [21]. The initial SiNTs are possibly composed of fourfold coordination silicon atoms. Three valance electrons in silicon atoms form a σ bond with electrons of other silicon atoms, while the fourth electron exists as a single dangling bond with hydrogen [7,22,23]. The single dangling bond with hydrogen assumed per silicon atom has been kept in the formation of SiNTs. Therefore, this model may explain in theory that initial SiNTs can form from SiO under supercritically hydrothermal conditions. The thermal stability of SiNTs is high according to the research using the empirical potential [23]. For the many-body empirical potential used, the binding energy is given as

$$E_{\text{bind}} = \sum_{i} \sum_{j>i} [V_R(r_{ij}) - B_{ij} V_A(r_{ij})] \tag{1}$$

where r_{ij} is the scalar distance between atom i and j, $V_R(r_{ij})$ and $V_A(r_{ij})$ represent a pair additive core-core repulsion and an attraction due to the valence electrons, respectively; B_{ij} is a many-body empirical bond order that couples quantities such as bond angles and local coordination to the attractive potential. Tersoff [24,25] has shown that a wide range of structural properties of materials including carbon and silicon can be appropriately described using this formalism if this function is used for the pair terms, providing a reasonable starting point for predicting trends such as thermal stability. This empirical potential is also a fit to the lattice constant and binding energy of a number of silicon lattices as well as the elastic constants and vacancy formation energies of graphite. Otherwise, the stability of SiNTs is high also possibly due to the high ratio of sp^3 to sp^2 hybridization. Furthermore, Kumar *et al.* [26] found that there was a mixed sp^2-sp^3 bonding character between Si atoms. The sp^2 bonding gives rise to the π conjugation of neighbor silicon atoms.

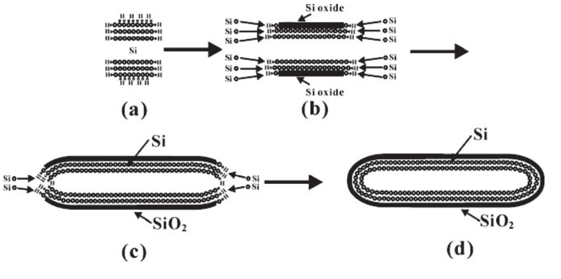

FIG. 5. SiNT Si-H model and self-assembled growth schematic of the SiNTs. (a) The formation of the initial SiNT under supercritically hydrothermal conditions. (b) Abundant Si atoms enter the initial SiNT resulting in the growth of the SiNT and the formation of silica outer layers retarding non-one-dimensional growth of the SiNT. (c) The formation of a closed cap of the SiNT. (d) The final formation of the SiNT.

SiO is less stable than the mixture of Si and SiO_2 and a disproportionation reaction of SiO proceeds with the following chemical formula: $2SiO \rightarrow Si + SiO_2$, where both the oxidation of Si[II] to Si[IV] and the reduction to Si[0] simultaneously occur [27]. So SiO is considered to discompose into Si and SiO_2 nanoparticles under the experimental conditions and a part of the Si nanoparticles are possibly gasified forming Si atoms under conditions of high temperature and high pressure. Abundant silicon atoms in the metastable state nucleate under the supercritically hydrothermal conditions and may result in the growth conditions to form the initial SiNTs following the SiNT Si-H model. Abundant dangling bondings existing in the surface of the initial SiNTs are saturated by hydrogen ions under the conditions with high temperature and pressure. It is well known that the saturation of the dangling bonds with hydrogen at the ends of SiNTs is crucial for the silicon tube to maintain a metastable structure preventing the SiNTs from deforming and eventually collapsing. Therefore, the dangling bondings with hydrogen atoms at the edge of SiNTs are possibly formed.

Si atoms are possibly formed owing to the high pressure and nucleation of Si atoms occurs with the increase of the temperature and pressure. A temperature field forms from the high temperature area at the inner wall of the kettle to the low temperature area in the center of the kettle with the increase of temperature. Initial Si tubular structures are likely to form through the nucleation stage of Si atoms due to the occurrence of the growth conditions to form the initial SiNTs following the SiNT Si-H model [Fig. 5(a)]. At the same time, the collision opportunity of the initial SiNTs and Si atoms increases because the initial tubular structures move continually between the high temperature area and the low temperature area under the stirring of the stirrer. Thus, abundant Si atoms continuously enter the tubular walls resulting in the one-dimensional growth along the temperature field direction. Si oxide reacts with the hydrogen in the surface of SiNTs forming stable silica outer layers and preventing the growth of SiNTs along the non-one-dimensional direction [Fig. 5(b)]. In addition, similar to the oxide-assisted growth mechanism of SiNWs [28], silica decomposed from SiO is also believed to play an important role, significantly enhancing the nucleation and one-dimensional growth of SiNTs. Some defects can also be observed from the HRTEM image as closed caps (Fig. 3). These defects could enhance the growth of SiNTs because defects are low energy states. The effect of dangling bondings with hydrogen in the growth edge of the SiNTs disappear gradually, changing the SiNTs from the metastable state to the stable state with the decrease of temperature and pressure. Simultaneously, the temperature gradient in the kettle also disappears gradually resulting in the closure of the growth end. Therefore, the growth of the SiNTs stops gradually [Fig. 5(c)]. A cap is finally formed due to the closure of the growth edge of the SiNTs [Fig. 5(d)].

In summary, the formation of self-assembled SiNTs without catalysts from silicon monoxide under hydrothermal conditions is demonstrated in this study. TEM and HRTEM images show that the SiNTs have closed caps. The structures of self-assembled SiNTs are hollow inner pore, crystalline silicon wall layers, and 2–3 nm amorphous silica outer layers. Amorphous silica outer layers can be removed after etching SiNTs with 5% HF acid for enough time. The possible reason for the formation of initial SiNTs is proposed and the growth mechanism of SiNTs is explained according to the SiNT Si-H self-assembled growth model. The synthesis of self-assembled SiNTs will open a new area to revise corresponding theory and develop potential applications of SiNTs.

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