

Formation of Silicon Carbide Nanotubes and Nanowires via Reaction of Silicon (from Disproportionation of Silicon Monoxide) with Carbon Nanotubes

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Abstract: One-dimensional silicon-carbon nanotubes and nanowires of various shapes and structures were synthesized via the reaction of silicon (produced by disproportionation reaction of SiO) with multiwalled carbon nanotubes (as templates) at different temperatures. A new type of multiwalled silicon carbide nanotube (SiCNT), with 3.5–4.5 Å interlayer spacings, was observed in addition to the previously known β -SiC (cubic zinc blende structure) nanowires and the biaxial SiC–SiO_x nanowires. The SiCNT was identified by high-resolution transmission microscopy (HRTEM), elemental mapping, and electron energy loss spectroscopy (EELS). The multiwalled SiCNT was found to transform to a β -SiC crystalline structure by electron beam annealing under TEM.

Introduction

Since the discovery of carbon nanotubes (CNT)¹ in 1991, the fabrication of nanometer-scaled one-dimensional materials has attracted considerable attention because of their potential use in both mesoscopic research and nanodevices. In particular, carbon nanotubes open up new and exciting possibilities for making different kinds of nanosized heterostructures by filling the inside hollow space with other elements or by decorating the outside surfaces of the nanotubes. For example, silicon carbide,^{2,3} gallium nitride nanowires,⁴ Si–B–C–N nanocables,⁵ heterostructures of carbon nanotubes and carbide nanorods,⁶ and SiC–SiO_x biaxial nanowires⁷ have recently been synthesized using carbon nanotubes as templates. These fabrication methods using carbon nanotubes as templates are highly promising due to the morphological integrity of carbon nanotubes which

spatially confine the reaction to the nanotubes. The net result is the formation of one-dimensional products with diameters, lengths, and orientations similar to those of the carbon nanotube templates.³

Recently, we developed an oxide-assisted growth method for the synthesis of bulk quantities of highly oriented silicon nanowires (SiNWs) by the thermal evaporation of silicon monoxide in a tube furnace.⁸ In this method, SiO powder was placed in the center of a tube furnace and heated above 1200 °C. The SiO vapor was transported downstream to a lower temperature zone (800–1000 °C) of the tube by a carrier gas wherein the SiO vapor disproportionates to Si and SiO₂ clusters. Under suitable growth conditions, the Si and SiO₂ clusters grow to form Si nanowires of tens of nanometers in diameter sheathed by a SiO₂ layer of a few nanometers in thickness. It occurs to us that this thermal evaporation method can be used as a suitable Si source to grow a wide variety of one-dimensional products containing silicon if other elements are introduced into the system, either as reactants or as templates. Among the various semiconducting materials, silicon carbide (SiC) possesses unique physical and electronic properties which make it a suitable material for the fabrication of electronic devices for high-temperature, high-power, and high-frequency applications.⁹ One-dimensional SiC nanosystems may exhibit unique properties due to quantum-size effects, making them useful materials in nanotechnology and nanoscale engineering. We report herein the growth of several kinds of one-dimensional nanostructures

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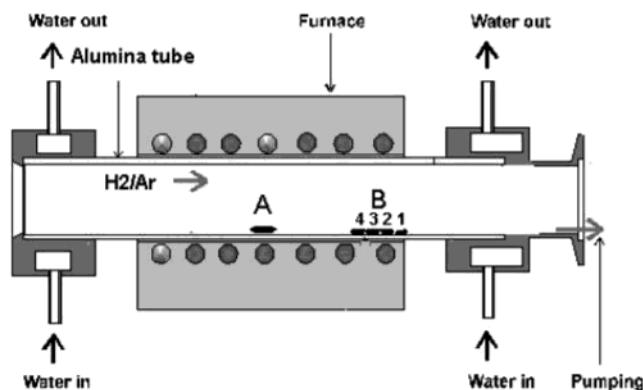


Figure 1. The schematic diagram of the synthesis apparatus.

of SiC via the disproportionation reaction of SiO with carbon nanotubes (as templates) in a tube furnace. Among the various SiC nanostructures (including β -SiC nanowires, biaxial SiC–SiO_x nanowires) that were formed, SiC nanotubes were observed for the first time.

Experimental Section

The equipment used for the present work is similar to that described previously for the growth of silicon nanowires (Figure 1). An alumina tube was mounted inside a tube furnace. The SiO powders (Aldrich, 99.95%) were placed at position A, the middle of the high-temperature zone of the furnace. Four pieces of silicon substrates on which

multiwalled carbon nanotubes (MWCNTs) had been grown were placed at positions marked B1–B4. MWCNTs of 10–50 nm in diameters were grown with iron particles as catalysts. They were grown vertically to the silicon chip substrate and had an aligned orientation. The four substrates were marked B1, B2, B3, and B4 according to their distances from the source, as indicated in Figure 1. The tube had previously been evacuated to a base pressure of 10^{-2} Torr by a mechanical pump. The carrier gas of argon mixed with 5% H₂ was introduced at one end of the alumina tube flowing at 50 sccm (standard cubic centimeters per minute) and at 500 Torr. The temperature of the furnace was increased to 1250 °C and kept at this temperature for 40 min. The temperatures at the substrate positions B4, B3, B2, B1 were found to decrease from 980 to 850 °C on the basis of a calibration curve. The products were examined by scanning electron microscopy (SEM, Philips XL 30 FEG). Detailed morphological and structural characterizations were carried out by using high-resolution transmission electron microscopy (HR-TEM) (Philips CM200 FEG), operated at 200 kV accelerating voltage at room temperature. Selected specimens were examined with electron energy loss spectroscopy (EELS) (Gatan GIF 200) and elemental mapping facilities, which were attached to the HRTEM operating at 200 kV.

Results and Discussion

The SEM results showed that products at position B1 consisted mostly of aligned carbon nanotubes along with few silicon nanowires. For positions B2 and B3, relatively more silicon nanowires were obtained on the top of the carbon

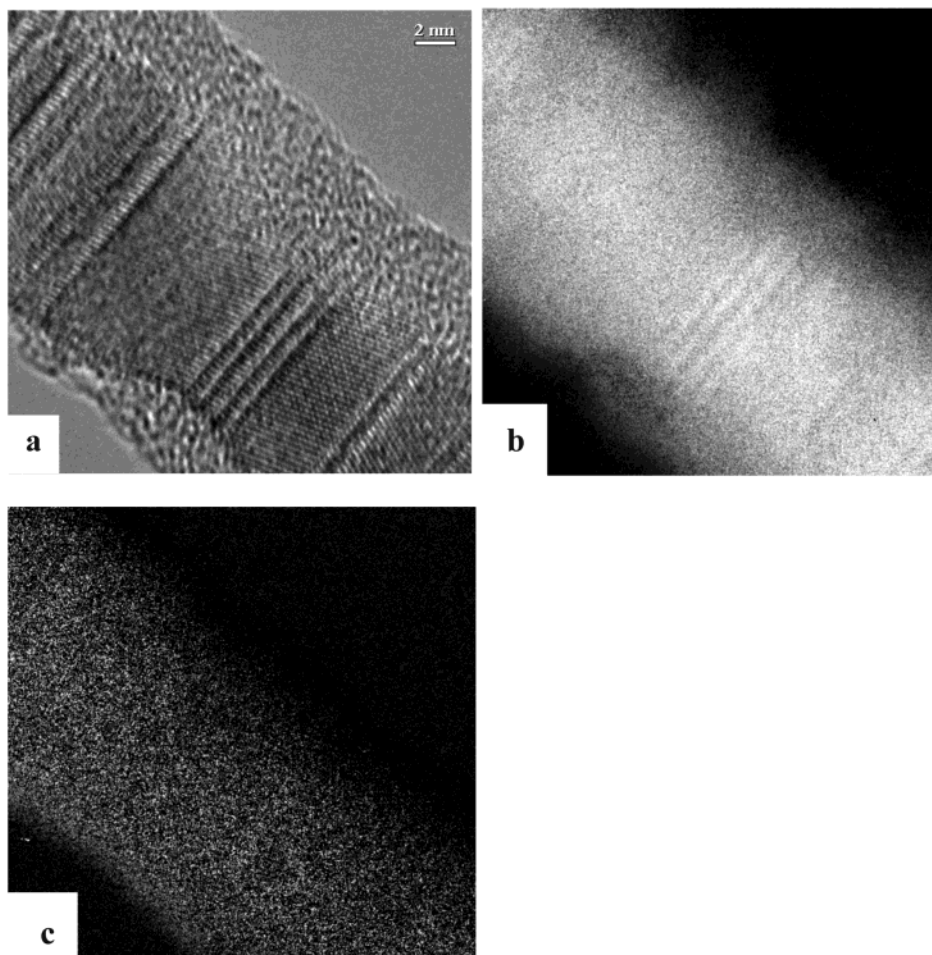


Figure 2. (a) The HRTEM image of SiC nanowires from reaction between silicon and carbon nanotubes. (b) and (c) Si and C element mapping of SiC nanowire in (a), respectively.

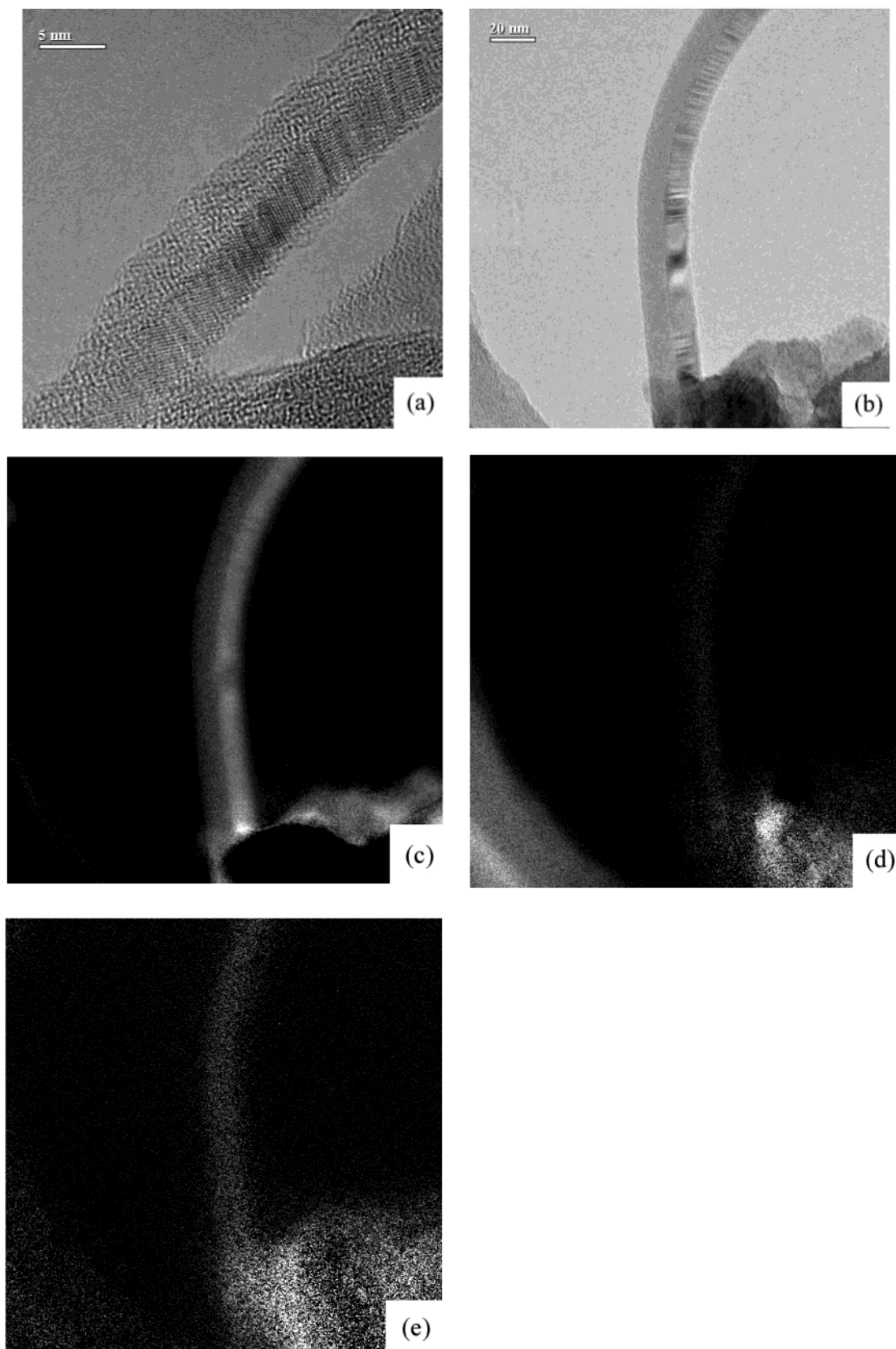


Figure 3. (a) The HRTEM image and (b) TEM image of the biaxial SiC–SiO_x nanowires from reaction between silicon and carbon nanotubes. (c), (d), (e) Si, C, and O element mappings of biaxial SiC–SiO_x nanowires in (b), respectively.

nanotubes. For position B4, the carbon nanotubes were almost completely covered with silicon nanowires.

Similar observation can be made from the TEM results. In other words, silicon nanowires were observed in all substrate

positions, but the quantities of the SiNWs increased from B1 to B4. Only very little SiNWs were obtained at B1 along with the unreacted carbon nanotubes. In contrast, for position B4, a large number of silicon nanowires with thick oxide layers were

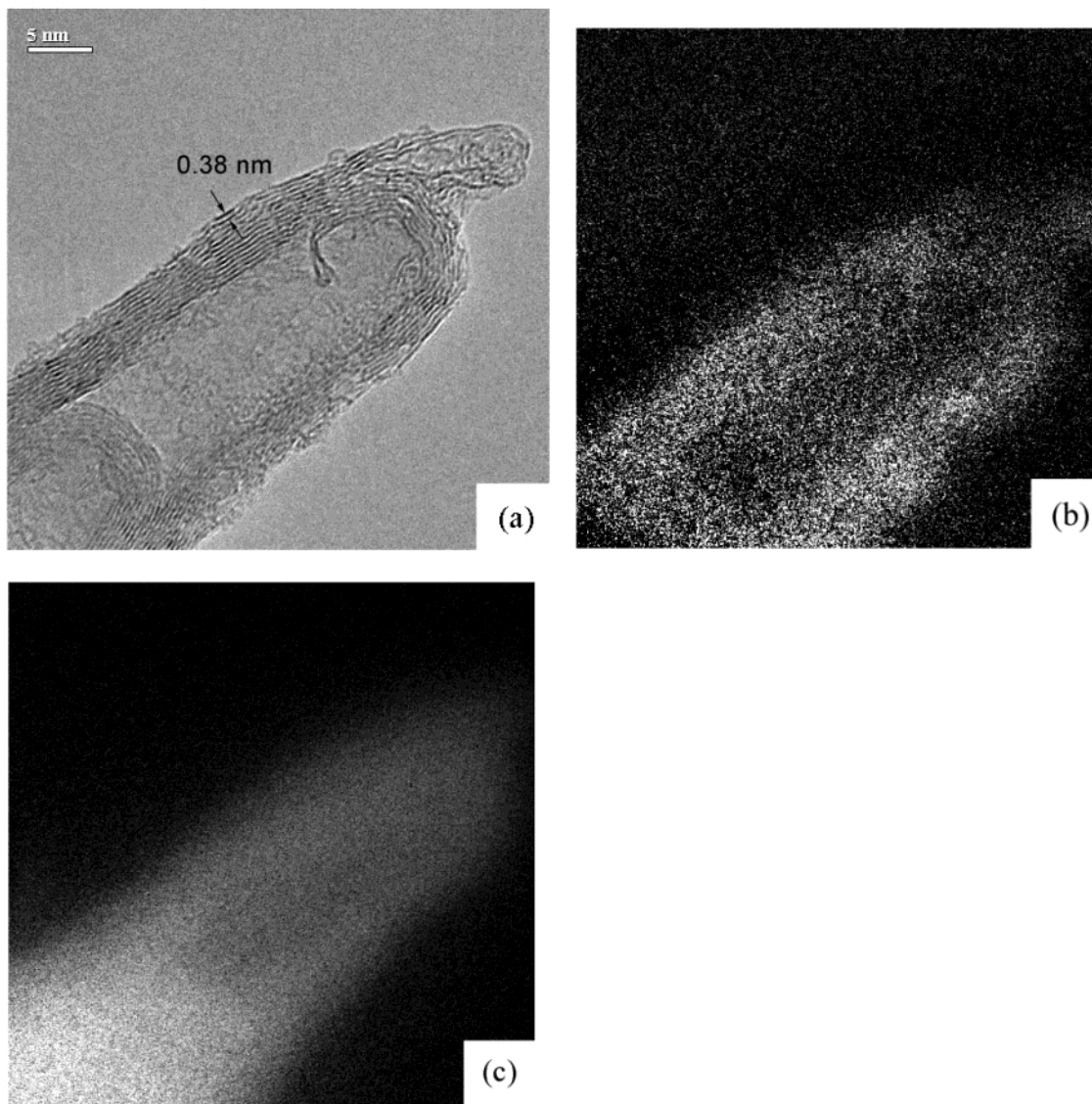


Figure 4. (a) The HRTEM image of an SiC nanotube structure with 3.8 Å spacing. (b) and (c) Si and C element mappings of an SiC nanotube in (a), respectively.

obtained. The most interesting products were obtained at position B3. Here, in addition to the SiNWs, many new structures were observed at B3 where the temperature was estimated to be about 935 °C. First, many silicon carbide nanowires with 2.5 Å spacing of the {111} planes of β -SiC with the cubic zinc blende structure (Figure 2a) were obtained. The C and Si elemental mappings of this nanowire are shown in Figure 2b and c, respectively. The result is in accord with the report of Z. Pan et al.³ The second structure obtained is the biaxial nanowires of silicon carbide–silicon oxide (Figure 3a and b). A similar biaxial structure had been observed by Z. L. Wang et al. using a similar method.⁷ The C, Si, and O elemental mapping of this nanowire (Figure 3c–e) confirmed the SiC–SiO_x biaxial structure. The biaxial SiC–SiO_x nanowires consist of two side-by-side sub-nanowires of β -SiC and silica, which can be simply referred to as a composite nanowire. In these SiC nanowires, there are many plane defects and stacking faults. The existence of stacking faults is consistent with the assumption that the SiC was formed through a solid–gas reaction of C and SiO.¹⁰

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Among the products obtained at position B3 was a new nanostructure which may be described as a multiwalled SiC nanotube. A typical image is shown in Figure 4a and Figure 5a. Element mappings (Figure 4b,c and Figure 5b,c) showed the multiwalled tube structure to be composed of Si and C. No oxygen was found in the structure. Furthermore, the interplanar spacings of these new Si-containing multiwalled nanotubes are significantly larger than 3.4 Å normally observed for the multiwalled carbon nanotube (for example, 3.8 Å in Figure 4a and 4.2 and 4.5 Å in Figure 5a). These observations suggest that the tubelike structures are not multiwalled carbon nanotubes. Instead, they are best described as a new type of multiwalled SiC nanotube (SiCNT) grown on a MWCNT (as template).

The EELS result (curve a in Figure 6) of a single multiwalled SiCNT shows that the Si L_{3,2}-edge shifts to a higher energy at 101.2 eV (from 99.3 eV of pure silicon) and the C K-edge shifts to a lower energy at 282.5 eV (from 284 eV of pure carbon), indicating a strong chemical bonding between Si and C. This is to be expected on the basis of the fact that carbon is more electronegative than silicon. The EELS of SiCNT is contrasted

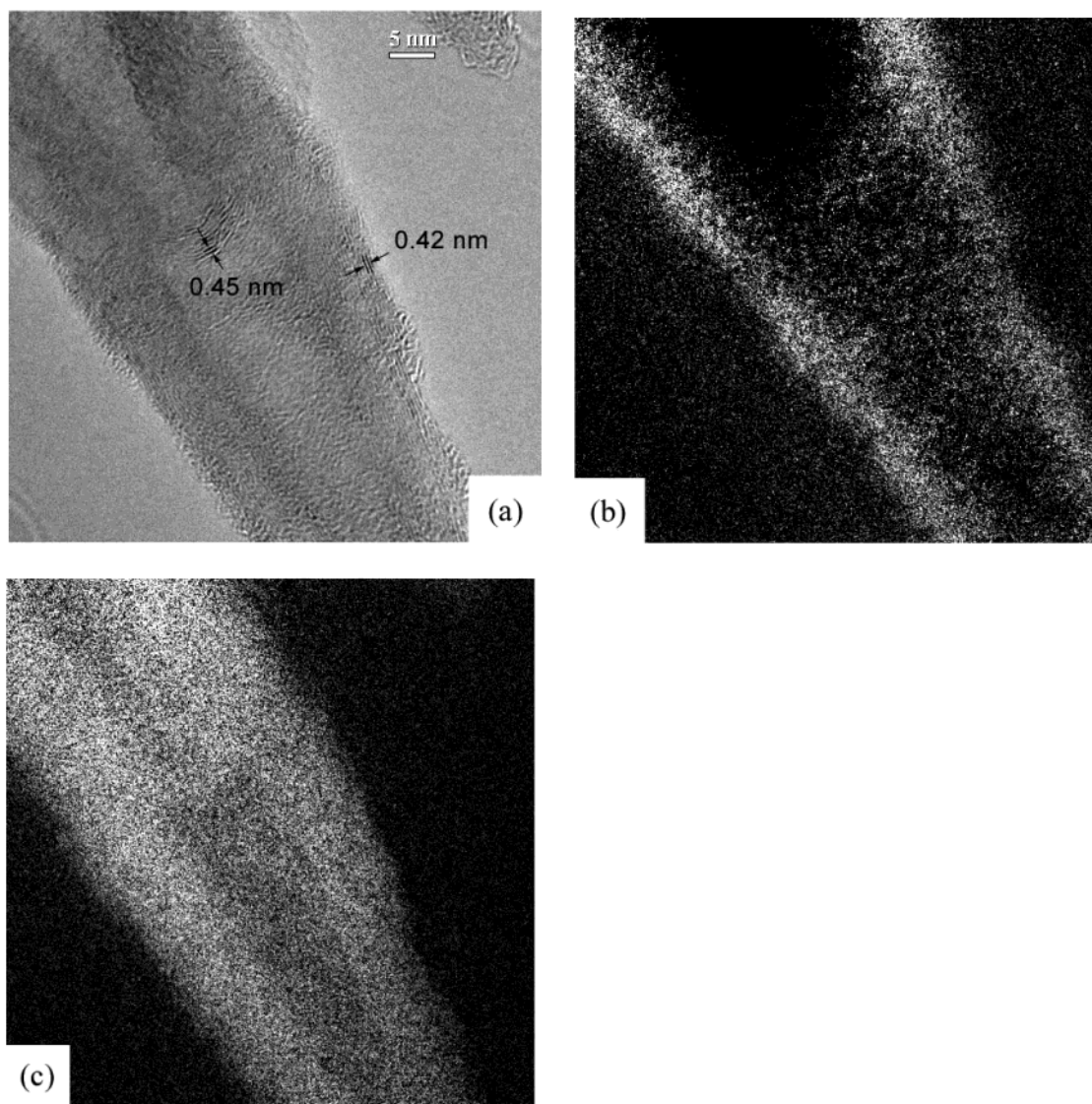


Figure 5. (a) The HRTEM image of the SiC nanotube structure with 4.2 and 4.5 Å spacings. (b) and (c) Si and C element mappings of an SiC nanotube in (a), respectively.

with the EELS of the β -SiC nanowire (curve b in Figure 6). With the exception of the preedge peaks, the two EELS spectra are rather similar. The strong preedge absorption peaks of both the Si and the C EELS of SiCNT (curve a of Figure 6) are indicative of the π bonding between Si and C (compare with curve b of Figure 6 for β -SiC). It is known that silicon carbide can form when Si meets C at a sufficiently high temperature (T) (roughly $T > 800$ °C).⁶ The temperature at B3 is around 935 °C, and in this temperature Si and C can react to form SiC. The transformation of a carbon nanotube to a carbide is controlled by the diffusion of Si to the SiC/C interface. However, the Si diffusion rate through bulk SiC is extremely slow in the temperature range of 800–1000 °C. A continuous supply of Si atoms from disproportionation of SiO is therefore transported primarily via surface diffusion.¹¹ Figure 7a showed that the interlayer spacings of the outer layers of a thick multiwall nanotube were 3.6 Å. Si elemental mapping in Figure 7b revealed that Si mainly resides in the boundary or outer layers,

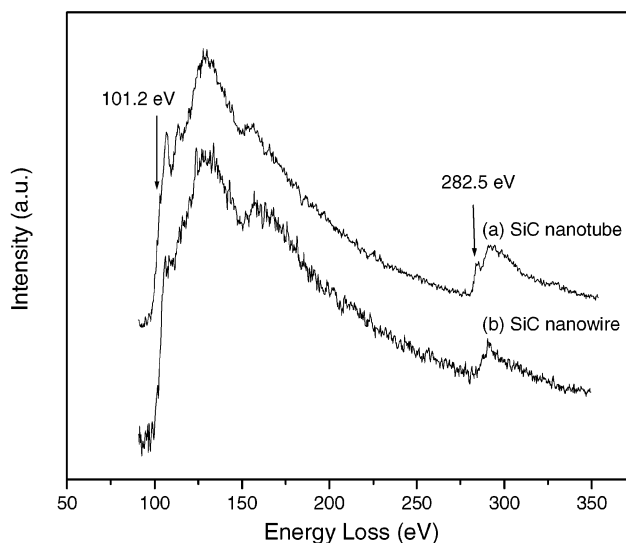


Figure 6. EELS spectra of (a) a single SiC nanotube and (b) a single SiC nanowire. Both were found in the B3 sample.

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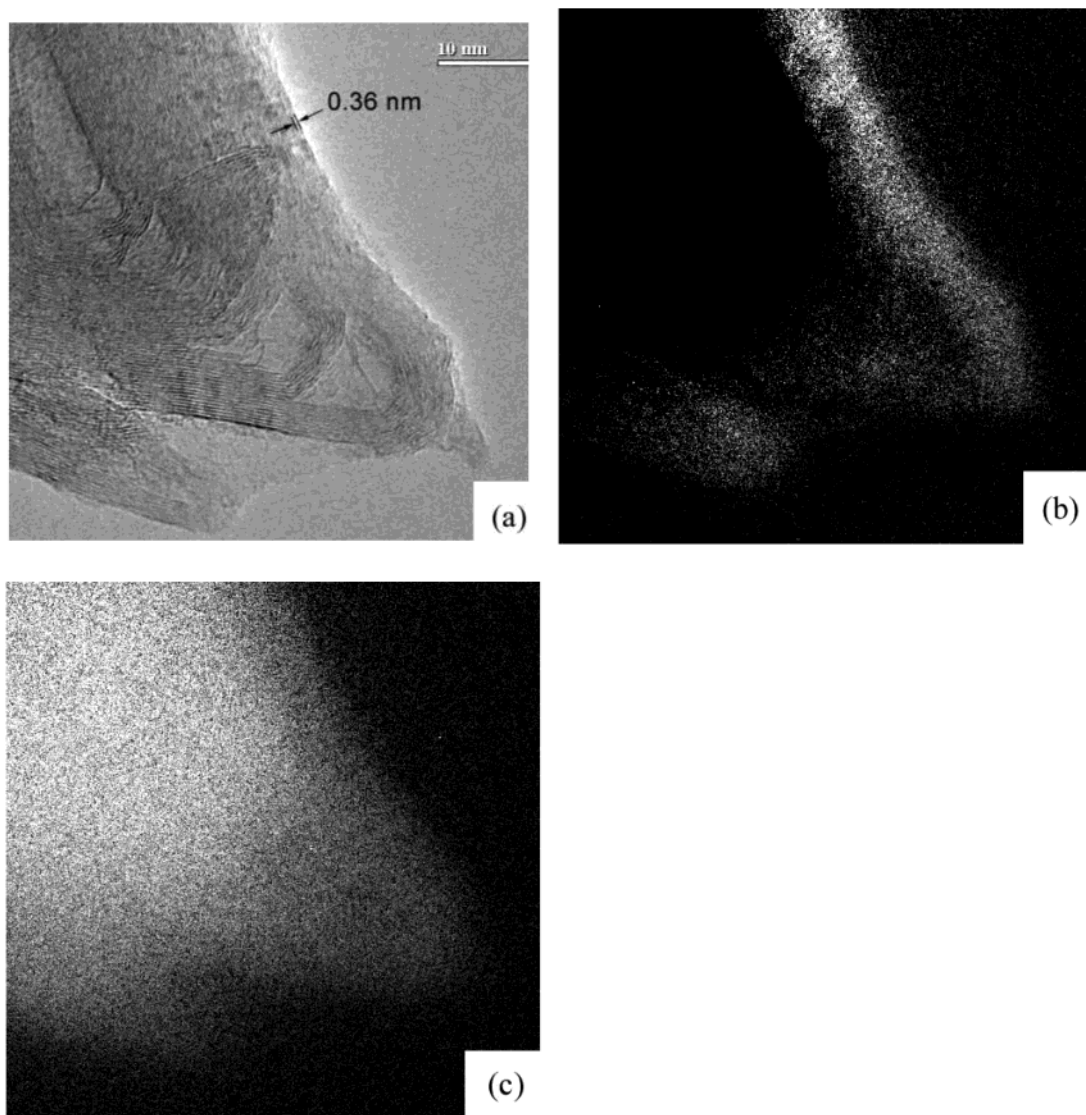


Figure 7. (a) The HRTEM image of a thick multiwall carbon nanotube with several SiC outlayers. (b) and (c) Si and C element mappings of an SiC nanotube in (a), respectively.

while the C elemental mapping in Figure 7c shows C distribution both in the inner region and in the outer layers of the tube. No silicon was found in the central hollow space or the inner regions of the MWCNT. Taken together, these observations suggest that the outer layers of the thick multiwall nanotube in Figure 7a were transformed to a multiwall SiC nanotube structure, while the inner part remained carbon nanotube. This is consistent with the notion that the SiC was formed layer by layer via surface diffusion of Si atoms into the carbon nanotube. We propose that, under our experiment conditions, the SiC nanotube structure may be a precursor to the SiC nanowires described above.

Additional evidence for the new multiwall SiC nanotube structure comes from an electron beam annealing experiment under TEM. A multiwalled SiCNT with 3.5 Å interlayer spacing was exposed to a convergent 200 kV electron beam of 32 nm in spot size and 100–150 μA in current for 15 s to 5 min continuously. Figure 8a–h recorded the annealing process. Before the electron beam annealing, the multiwall nanotube structure was identified by Si and C elemental mappings to be a SiC nanotube as described above. After the first 15–30 s of annealing, the nanotube structure began to collapse, and the

layer planes started to curl and bend, as shown in Figure 8b and c, respectively. After 45 s of annealing, the onionlike structure shown in Figure 8d with 3.3 Å interlayer spacing was formed. After 1 min (Figure 8e), the layers of the onionlike structure began to curl and self-compress; eventually the interlayer spacing was reduced to 3.2 Å. After 2 min (Figure 8f), the onionlike structure was broken, and the interlayer spacing continued to compress. After 5 min (Figure 8g), a crystalline structure, with the 2.5 Å *d* spacing of the {111} planes of β-SiC (Figure 8h), was eventually formed. The ultimate formation of β-SiC provides further evidence that the nanotube structure before annealing was indeed an SiC nanotube. We note that the transformation from a carbon nanotube to diamond was induced by electron irradiation with an acceleration voltage of 1.25 MeV and heating the sample stage to 700 °C under TEM as observed by F. Banhart et al.^{12,13} Under such severe experimental conditions, the graphitic cores of the onions were found to undergo a phase transition to diamond as a result of self-compression.¹³ In our case, the transformation of an SiC

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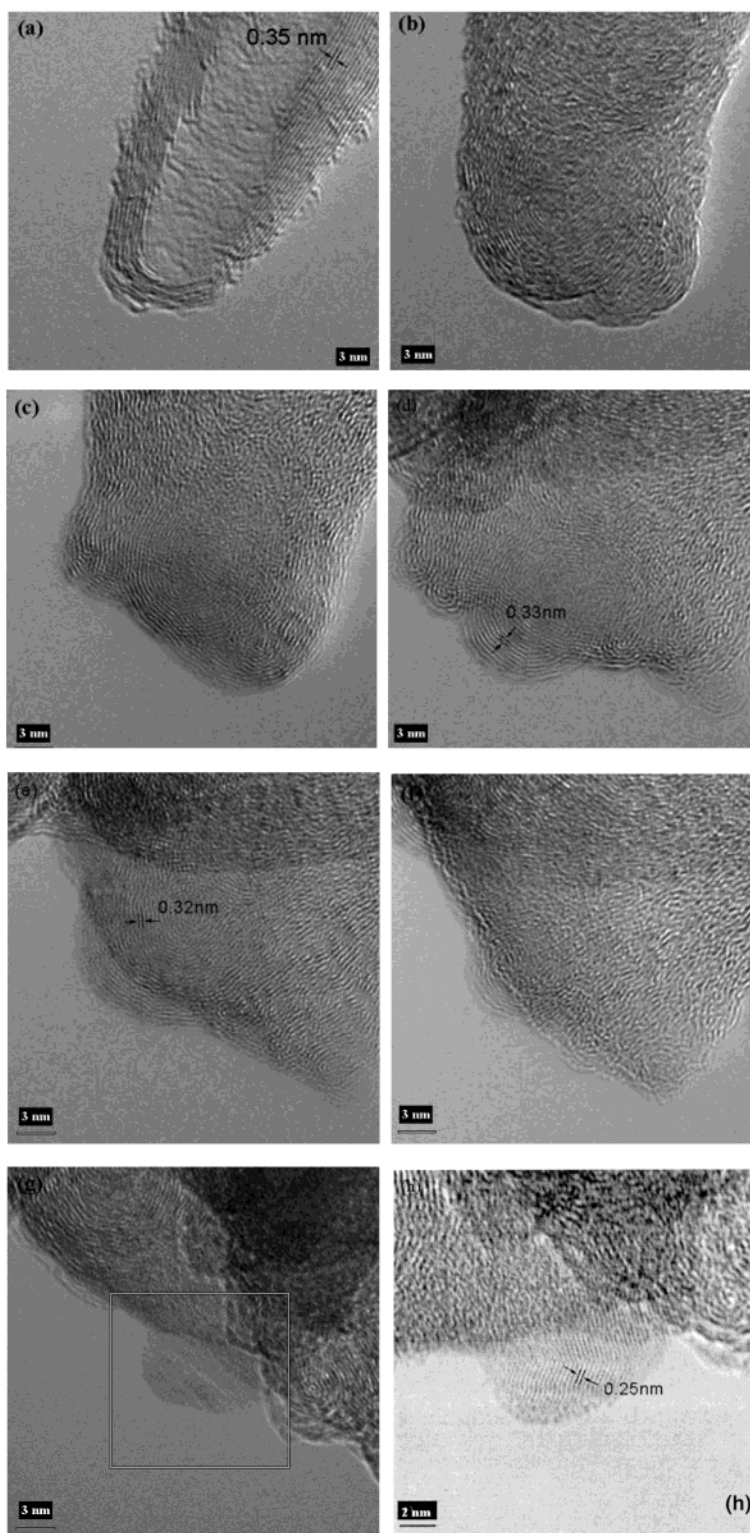


Figure 8. The HRTEM images of the electron beam annealing process of an SiC nanotube: (a) before annealing, (b) after 15 s, (c) after 30 s, (d) after 45 s, (e) after 60 s, (f) after 2 min, and (g) after 5 min of annealing; (h) zoom-in image of (g).

nanotube to the β -SiC structure requires only 200 keV electron beam irradiation under normal TEM operating temperature (i.e., without heating). It's possible that, under our reaction conditions, the SiC nanotube structure is an intermediate/metastable phase in the reaction between carbon nanotubes and silicon to form the β -SiC nanowires. On the basis of these observations, we conclude that the observed multiwalled SiC nanotube is a new polytype of SiC, with interlayer spacing ranging from 3.5–4.5

Å, distinct from amorphous SiC or any of the common crystalline SiC phases such as cubic (3C), hexagonal (4H, 6H), or rhombohedral (15R) structures, etc. We propose the structure of this new multiwall SiC nanotube to be similar to that of the carbon nanotube with the Si atoms substituting for half of the C atoms in the curved hexagonal graphite tube structure. Work is in process to further the understanding of the detailed structures of these SiC nanotubes.

In summary, different silicon–carbon nanostructures were synthesized by decomposing SiO on multiwalled carbon nanotubes (as templates) in different temperature zones. In addition to the β -SiC nanowires and the biaxial SiC–SiO_x nanowires, a new type of multiwalled silicon carbide nanotubes, with interlayer spacing ranging from 3.5–4.5 Å, was observed resulting from the reaction of silicon (via disproportionation of SiO) and multiwalled carbon nanotubes (as templates). It should be emphasized that the evidence presented in the paper is mainly morphological (from TEM), which indicates that multiwalled nanotubes with interlayer spacings different from the conventional carbon nanotubes are present and that there are carbon and silicon (from elemental mapping) in the outer layers of the nanotubes' structure. Further supporting evidence of the new nanostructure came from the EELS measurements of single

tubes. Work is in progress to provide further information regarding the atomic and/or electronic structures of this new type of silicon carbide nanostructure.

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