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Production of Aligned Carbon Nanotube Films and Nitrogen Doped Carbon Nanotube Films from the Pyrolysis of Styrene
Substitution reactions of carbon nanotube template

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Substitution reactions between carbon nanotube (CNT) template and SiO with the formation of carbon rich silicon oxide nanowires (SiO–C-NWs) have been investigated using transmission electron microscopy and x-ray energy dispersive spectroscopy. The reaction was carried out by thermal annealing at 1200 °C for 1 h of a mixture of silicon monoxide (SiO) and iron (II) phthalocyanine, FeC32N8H16 (FePc) powders. Multiwalled CNTs were produced first via pyrolysis of FePc at a lower temperature (1000 °C). SiO vapors reacted with the CNTs at higher temperatures to produce amorphous SiO–C-NWs with a uniform diameter and a length in tens of micrometers. The special bamboollyke structure of the CNTs allows the reaction to start from the external surface of the tubes and transform each CNT into a solid nanowire section by section. © 2006 American Institute of Physics. [DOI: 10.1063/1.2208548]

Carbon nanotube (CNT) is an important one-dimensional nanomaterial, and can also be used as a template for the formation of other one-dimensional nanostructures. A large range of nanotubes and nanowires has been synthesized using CNTs as the template.1–8 The role of the CNTs is to act as a skeleton of the tubular structure for nonlayered materials which cannot form tubular structures directly. For example, boron nitride nanotubes were formed via direct substitution reactions between CNTs and boron oxides.1 Both tubular structure and size are maintained.1–4 NbS2 nanotubes are deposited on the external surface of the CNTs,5,6 and the diameter of the composite nanotubes is larger than that of the original. In the case of nanorods and nanowires, the one-dimensional (1D) structure of the nanotubes constrains the growth of other materials into a 1D structure. Very thin nanowires and nanorods with a diameter of a few nanometers can be formed inside open-ended CNTs due to capillarity effects, and the diameter of the nanorods is limited by the inner diameter of the nanotube.7 There is no chemical reaction between the CNTs and the filling nanorods. The nanorods can be purified by burning the carbon template away in air. A more versatile way to produce a large range of nanowires and nanorods using CNT templates is via substitution reactions with the template nanotubes.7,8 The tubular structures are often replaced by solid wires with the same size. Although a large number of successful CNT-template syntheses have been reported, the substitution reactions and the 1D structural changes have not been carefully investigated. In this letter, we report a detailed investigation on the substitution reaction between SiO vapor and CNTs with the formation of carbon rich silicon oxide nanowires (SiO–C-NWs) as the end product. The reaction process and a model are described based on transmission electron microscopy (TEM) observation.

Pure silicon monoxide (SiO) (Aldrich, 325 mesh, 99.9%) and iron (II) phthalocyanine, FeC32N8H16 (FePc) (Aldrich, CAS Number: 132-16-1) powders were mixed together at a weight ratio of 1:1 in a quartz mortar. The mixed powder was loaded into a ceramic combustion boat, which is inserted in the center of an alumina tube furnace. The furnace tube was flushed with a mixed Ar, H2 (5%) gas at a flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP). Several Si wafers were placed near the combustion boat downstream direction to collect depositions using carrier gas, again Ar, H2 (5%). The furnace was first held at 1000 °C for 30 min. After removing one Si wafer as a monitor of deposition at 1000 °C, the temperature was then raised to 1200 °C and held for 1 h. The annealing was terminated by cooling the furnace to room temperature in the same gases. Thin deposition layers were formed on Si wafers. The structures of the deposits were characterized by field emission scanning electron microscope (FESEM) (Hitachi, S-4500 operated at 3 kV) and high-resolution transmission electron microscope (HRTEM) (Philips, CM 300 operated at 300 kV). The chemical compositions were examined using x-ray energy dispersive spectroscopy (EDS) (retractable EDAX SUTW detector fitted to the CM 300).

During the annealing at 1000 °C, CNTs grew on the Si wafer located 5 cm away from the center of the boat where the temperature was in the range of 700–800 °C, calibrated by a thermocouple before annealing.9 The SEM image in Fig. 1(a) shows a high density of randomly oriented CNTs with an average diameter of about 140 nm and a length of more than 20 μm. The TEM image in Fig. 1(b) reveals that a multiwalled and bamboollyke structure is produced from the elongated Fe particle on its tip, which has been investigated previously.10–12 The lattice image in the insert of Fig. 1(b) shows some graphic layers terminating along the nanotube external surface indicated by the arrows. Similar CNTs were assumed to have formed on the surface of the other Si wafers at the same temperature zone. After annealing at 1200 °C for 1 h, a white deposit was present on the Si substrates. The temperature of deposition was between 900 and 1000 °C. Large quantities of nanowires with a random orientation and
a uniform diameter were found using SEM, as shown in Fig. 1(c). No particle or coating on the surface of the wires could be found. The TEM image shown in Fig. 1(d) reveals a solid wire attached to a round Fe particle at the tip. The average diameter of this kind of nanowire is about 140 nm and the typical length is more than 20 μm, which is like the size range of the CNTs. This kind of nanowire is amorphous as evidenced by the selected area electron diffraction (SAED) pattern inserted in Fig. 1(d). The EDS spectra taken from the body of the nanowire crossing a hole in the carbon support film show that the chemical compositions include Si, O, and C (Cu x rays come from the copper support grid for the TEM sample).

The multiwalled CNTs can be grown by pyrolysis of FePc in the temperature range of 800–1100 °C. The Fe in FePc plays a catalytic role via the vapor-liquid-solid (VLS) growth mechanism. Because this temperature range is below the vaporization temperature of the SiO powder (1100–1400 °C), SiO powders remain solid in the boat. As the temperature increased up to 1200 °C, the SiO powder vaporized and the vapors were flushed by the carrier gas to the Si wafers in the downstream direction. As these vapors reached the CNTs formed previously, they reacted with the CNTs to form solid SiO–C-NWs maintaining 1D shape.

To investigate the above reaction process, the nanowires with a mixed structure of CNT plus amorphous SiO–C-NWs were grown in a lower temperature zone further downstream (7 cm away) from the center of the boat where the temperature was around 800–900 °C during the nanowire formation. The TEM image in Fig. 2(a) shows a nanostructure with a hollow tubular structure grading into a solid wire structure with essentially constant diameter. The lattice images in Figs. 2(b) and 2(c) were taken from the two different areas marked with “B” and “C” in Fig. 2(a), respectively. It can clearly be seen in Fig. 2(b) that the graphitic layers are still crystalline near the inner tube surface while the outer layers have been converted to amorphous SiO–C-NWs of a few nanometer thick. The other part of the wire completely converted to solid amorphous materials is shown in Fig. 2(c). The TEM observation [Fig. 2(b)] suggests that the chemical reaction started from the external surface of the CNTs. In the case of AlN formation from a CNT template, the nitriding reaction starts from the inner surface of the CNTs because of the opened ends. In the current case, the CNTs have the special bamboolike structure; the hollow tube is segmented by many thin walls so that SiO vapor cannot diffuse inside the tubes.

The terminations of graphitic layers along the nanotube external surface [Fig. 1(b) insert] provide more active sites for the substitution reactions. Consequently, the substitution reactions proceed along the nanotubes as Figs. 2(a) and 2(c) show. At very high temperatures (1600 °C), equivalent substitution reaction can take place on the smooth external surface of multiwalled cylindrical CNTs with Al2O3 vapor.

When the reaction proceeds further, even deeply buried graphitic layers react with SiO vapors. The bamboo template of the CNTs is completely destroyed. Clearly there has been an increase in solid volume since that internal cavity has been eliminated. A calculation of the relative number of C atoms per nanometer length in CNT relative to that in
SiO–C-NWs can provide some constraints on the reaction that has occurred.

Assume all the C atoms in CNT with external diameter of 70 nm and internal cavity of 35 nm diameter are in the graphite structure, and in the solid, 70 nm diameter SiO–C-NWs of stoichiometry SiO:C is 1:1.

From the calculation indicated in Table I, the number of the C in SiO–C-NW is about six times less than that in the original CNT. There are several simple ways to interpret this result. Firstly, some C may have reacted with O to form volatile CO, or CO2, partially destroying the CNTs. In this case, the CNT diameter should have reduced. Secondly, the density from bulk amorphous Si–O–C (Ref. 16) could be too low for the SiO–C-NW material, but presumably not by anywhere near as much as 6, probably not even as much as 1.5, so this explanation alone also appears unlikely. Thirdly, the stoichiometry of the amorphous wire could be much more C rich than SiO:C of 1:1—this could be quite likely since the starting material contained no SiO.

A simple calculation of mass gives another perspective—using densities and sizes in Table I, the unit length of CNT weighs 2.65×10−17 g/nm length while the SiO–C-NW is 2.0×10−17 g—so significant mass has been lost, even though the external diameter has not changed and the internal cavity has disappeared. A conclusion can be tentatively made about the SiO–C-NWs, even though there are too many unknowns, that C loss must have occurred and that the SiO:C is really ≈1 if SiO–C-NW density is limited to less than 1.5, probably not even as much as 1.5, so this explanation alone also appears unlikely. Thirdly, the stoichiometry of the amorphous wire could be much more C rich than SiO:C of 1:1—this could be quite likely since the starting material contained no SiO.

Because of the low growth temperature, the reaction between CNTs and SiO vapors has not proceeded to the stable end products of SiC plus CO2. The amorphous SiO–C-NWs are thermally metastable and are expected to change into SiC with ball milling treatment before annealing.17 Although Fe particle plays the catalytic role in the CNT formation, the TEM observation does not find any involvement of Fe during substitution reaction. Similarly, the Si wafer has no role other than carrying the one-dimensional structures. The changes of the shape of the Fe particle from elongated to round are probably due to surface energy effects at the high temperature (1000 °C).

In summary, SiO–C-NWs have been produced using multiwalled CNTs as a template, which were synthesized by pyrolysis of FePc. The segmented bamboolike structure of the CNTs causes the reaction to start on the external surface of the tubes and progressively transform the CNTs into solid nanowire segment by segment. The relatively low annealing temperature results in metastable amorphous SiO–C instead of SiC nanowires. Fe appears not to be involved in nanowire formation or the substitution reaction.

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**TABLE I.** Comparison between CNT and SiO–C-NW of stoichiometry SiO:C=1:1.

<table>
<thead>
<tr>
<th></th>
<th>CNTs</th>
<th>SiO–C–NWs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.267</td>
<td>1.3³</td>
</tr>
<tr>
<td>Typical radius (nm)</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Typical radius (nm)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Volume (nm³)/nm length of tube or wire</td>
<td>1.15×10⁴</td>
<td>1.54×10⁴</td>
</tr>
<tr>
<td>No. of C atoms/nm length</td>
<td>1.31×10⁵</td>
<td>2.15×10⁵</td>
</tr>
</tbody>
</table>

³Reference 16.