



Continuous synthesis and characterization of silicon carbide nanorods

Weiqliang Han^a, Shoushan Fan^{a,*}, Qunqing Li^a, Wenjie Liang^a, Binglin Gu^a,
Dapeng Yu^b

^a Department of Physics, Tsinghua University, Beijing 100084, China

^b Department of Physics, Peking University, Beijing 100084, China

Received 3 August 1996

Abstract

A two-step reaction scheme has been employed for the synthesis of SiC nanorods at 1400°C. SiO vapour was generated via the silicon reduction of silica, and then this SiO vapor reacted with carbon nanotubes to form SiC nanorods. The morphology and structure of the nanorods were characterized by XRD, TEM, IR and Raman spectroscopy. The nanorods are single crystalline β -SiC with the diameters ranging from 3 to 40 nm. A broad photoluminescence peak located around 430 nm under 260 nm UV fluorescent light excitation at room temperature is observed. A growth model of SiC nanorods is proposed.

1. Introduction

SiC whiskers are effective materials for the reinforcement of various composite materials, mainly due to their superb mechanical properties. The benefits of incorporating such reinforcing agents in Al_2O_3 , Si_3N_4 , SiC and ZrO_2 matrices have already been demonstrated to yield enhanced toughness, strength, and creep performance [1–4]. However, the mechanical properties of the composite materials vary significantly with the surface chemistry and morphology of whiskers which depend on the method of production. SiC whiskers have been produced by several routes: carbothermal reduction of silica [5], decomposition of organic silicon compounds [6], and

reaction between silicon halides and CCl_4 [7]. Generally these whiskers have diameters of about half a micrometer. Recently, carbon nanotubes were used to make SiC whiskers. Zhou and Seraphin developed a process for producing SiC whiskers through a reaction between the carbon nanotubes and SiO, but the size of the SiC products were typically much larger than the carbon nanotubes [8]. However, Dai et al. successfully synthesized SiC nanorods whose diameters were similar to or much smaller than the diameters of the carbon nanotubes through a reaction between the carbon nanotubes and SiO or Si-I₂ [9].

In this work, a continuous process for the synthesis of SiC nanorods via a two-step reaction has been developed. These studies address the overall structure, properties and growth mechanism of SiC nanorods.

* Corresponding author. E-mail: fss-dmp@mail.tsinghua.edu.cn

2. Experimental procedures

The preparation apparatus for the continuous synthesis of SiC whiskers is a conventional furnace with a sintered alumina tube. The alumina crucible containing silica(68.2 wt%)-silicon(21.8 wt%) powder mixture was placed at the hot zone inside the alumina tube, and the carbon nanotubes were put on top of the Si-SiO₂ powder mixture. Argon gas was introduced to maintain the inert atmosphere during the overall reaction period. The reaction temperature was 1400°C.

Upon completing the reaction, the collected SiC nanorods were characterized by X-ray diffraction (Rigaku D/max-RB), high resolution transmission electron microscopy (Hitachi-9000NAR), infrared spectroscopy (Perkin Elmer 2000 FT-IR), Raman spectroscopy (Spex 1403), and photoluminescence spectroscopy (Perkin Elmer LS50B).

3. Results and discussion

After the heat treatment, the color of the reactant changed from black to light green. The result of an XRD spectrum (e.g., Fig. 1) shows that the products were predominantly β -phase of SiC. The carbon nanotubes used in this reaction were prepared by chemical vapour deposition method using ethylene and hydrogen [9]. The TEM image of the carbon nanotubes shows that the diameters of the carbon nanotubes range from 13 to 16 nm. The shell thicknesses of the carbon nanotubes, measured from HREM image, range from 4 to 6 nm (Fig. 2a). The

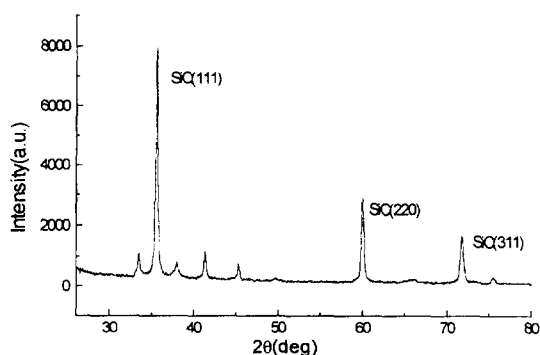


Fig. 1. XRD of SiC nanorods.

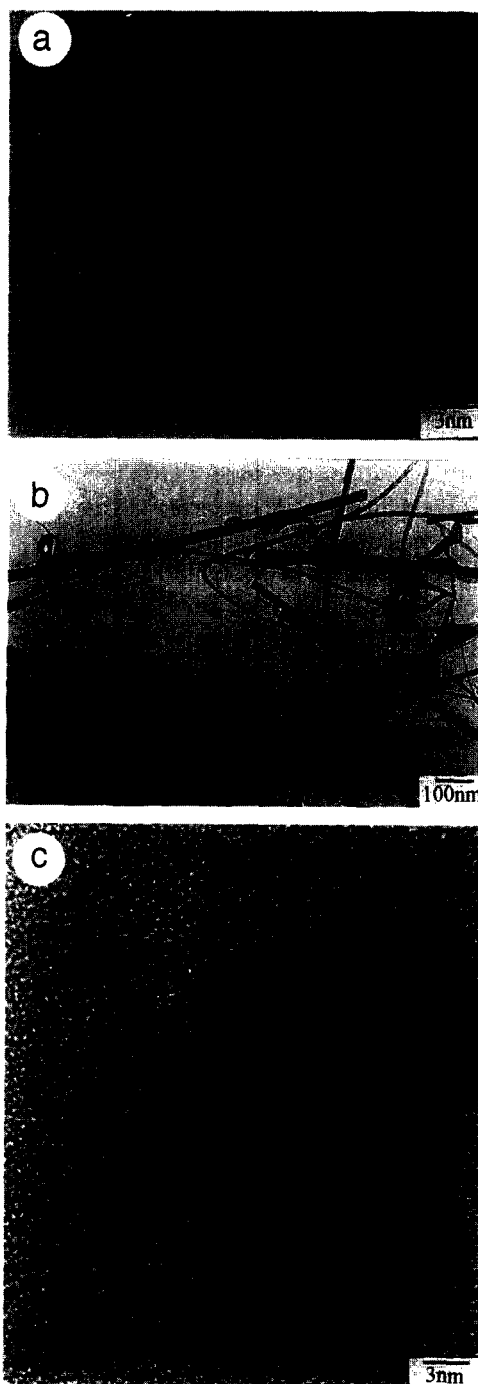


Fig. 2. (a) High-resolution transmission electron micrograph of carbon nanotubes. (b) TEM micrograph of SiC nanorods. (c) Lattice image of two SiC nanorods.

TEM image (Fig. 2b) reveals that the diameters of the SiC nanorods range from 3 to 40 nm which diverge from the diameters of the carbon nanotube precursors. The SiC nanorods are solid other than the hollow core structure of carbon nanotubes. The lattice image of two SiC nanorods is shown in Fig. 2c. The thinner SiC nanorod, which is just 3 nm in diameter, shows a high density of defect planes. These defect planes are basically rotational twins on the (111) basal planes. The side surfaces are pleated in microscale due to a tendency for the growing crystal to develop small facets on alternating {111}-type close-packed planes. The microfacets are typically associated with the presence of defect planes intersecting the whisker surface [10].

Fig. 3 shows the IR spectrum of the nanorods. The presence of an absorption peak at 814 cm^{-1} and the weak absorption at about 1100 cm^{-1} in the IR spectrum indicate the Si–C stretching vibration and the Si–O stretching vibration. Therefore, the produced nanorods consisted mainly of SiC with a minor amount of silicon oxides. Fig. 4 shows the Raman spectrum of the nanorods at room temperature after exciting with the 514.5 nm line of an argon ion laser. The presence of a sharp peak at 784 cm^{-1} in the Raman spectrum also shows that the nanorods are well crystalline β -SiC [11]. Fig. 5 shows the PL

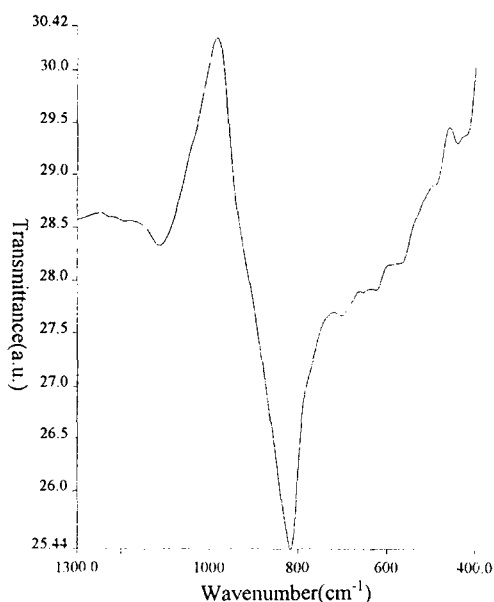


Fig. 3. IR spectrum of SiC nanorods.

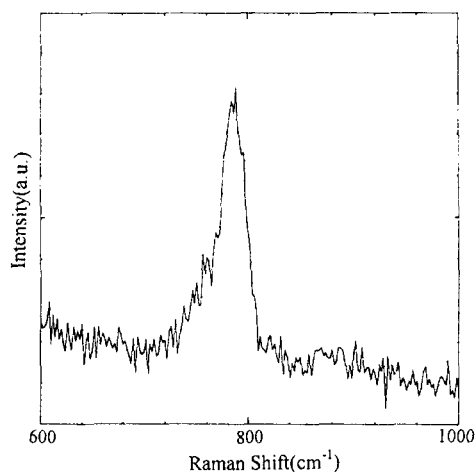
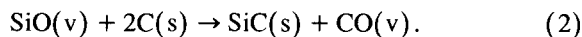
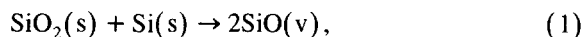


Fig. 4. Raman spectrum of SiC nanorods.

spectrum from the SiC nanorods at room temperature under 260 nm UV fluorescent light excitation. The PL peak wavelength is at 430 nm .

In the two-step reaction process, the reaction equations are



We have used the above reaction scheme to estimate the diameter of produced SiC nanorods. Suppose the diameter and the shell thickness of the carbon nanotube are D and A , respectively. The number of carbon atoms per unit length of carbon nanotube can be calculated from

$$N_C = (V_C \rho_C / M_C) N_A, \quad (3)$$

where $V_C = \pi[(D/2)^2 - (D/2 - A)^2]$ is the volume

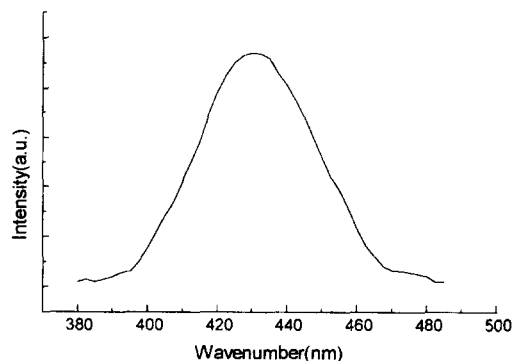


Fig. 5. PL spectrum of SiC nanorods.

per unit length of carbon nanotube. $M_C = 12$ g and $\rho_C = 2.26$ g/cm³ are the molar weight and the density of the carbon nanotubes, respectively. N_A is the Avogadro constant.

Suppose the diameter of the produced SiC nanorod is d . The number of carbon atoms per unit length of SiC nanorod can be calculated from

$$N_C^{\text{SiC}} = N_{\text{SiC}} = (V_{\text{SiC}} \rho_{\text{SiC}} / M_{\text{SiC}}) N_A, \quad (4)$$

where N_C^{SiC} and N_{SiC} are the number of carbon atoms per unit length of SiC nanorods and the number of SiC molecules per unit length of SiC nanorods, respectively. $V_{\text{SiC}} = \pi(d/2)^2$ is the volume per unit length of SiC nanorods. $M_{\text{SiC}} = 40$ g and $\rho_{\text{SiC}} = 3.2$ g/cm³ are the molar weight and the density of β -SiC, respectively.

During the reaction, the carbon nanotubes are the only carbon source involved. In reaction (2), only half amount of carbon atoms are used to form SiC and another half amount of carbon atoms are used to generate CO vapour. So we have

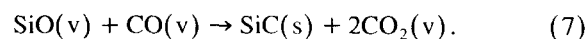
$$N_C^{\text{SiC}} = 0.5 N_C. \quad (5)$$

From the above equations, the diameter of the produced SiC nanorod d can be derived and represented as

$$d = \left(\frac{2[(D/2)^2 - (D/2 - A)^2] \rho_C M_{\text{SiC}}}{\rho_{\text{SiC}} M_C} \right)^{1/2}. \quad (6)$$

In the experiment, the diameters and shell thicknesses of the carbon nanotubes range from 13 to 16 nm and 4 to 6 nm, respectively. Using the values $D = 15$ nm and $A = 5$ nm, the diameter of SiC nanorods calculated from Eq. (6) is 15.3 nm. This means that the diameter of SiC nanorods should be almost equal to the diameter of carbon nanotubes. However, the measured diameters of the produced SiC nanorods range from 3 to 40 nm. The diameter divergence can be explained as follows.

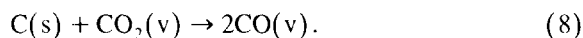
The generated CO vapour in reaction (2) could react with SiO vapour on the generated SiC nanorods surface by the reaction



In such a case, the epitaxial growth of SiC on the surface of initially produced SiC nanorods from reaction (2) make the diameter of some final SiC

nanorods larger than the diameter of the carbon nanotube precursors.

In contrast, when the CO₂ vapour generated from reaction (7) reaches the surface of carbon nanotubes, the following reaction could happen



This makes the diameter of some nanotubes much thinner than the diameters of the initial carbon nanotubes. Therefore the diameters of the SiC nanorods growing from these thinned carbon nanotubes are also much thinner than the diameters of the initial carbon nanotubes. In the meantime, the generated CO vapour from reaction (8) could be another reactive vapour source for reaction (7).

4. Conclusion

SiC nanorods are synthesized in a two-step process involving the generation of SiO followed by SiC growth. The SiC nanorods are basically single crystal cubic structures with diameters ranging from 3 to 40 nm. There is a broad photoluminescence peak located around 430 nm under 260 nm UV fluorescent light excitation at room temperature. The reason for the variation of the diameter of SiC nanorods from that of the carbon nanotube precursors is due to the different reactions among SiO, CO, CO₂ and C.

Acknowledgement

The authors would like to thank Professor Peiyi Chen for helpful discussions and Lishen Chen, Weigou Liao and Zhen Guo for their help in sample preparation and measurements. This work was supported by the National Nature Science Foundation of China.

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