Synthesis of SiC nanowires from gaseous SiO and pyrolyzed bamboo slices

Cui-yan LI, Jianfeng Huang, Liyun CAO, Jing LU
School of Materials Science and Engineering, Shanxi University of Science & Technology, Xi’an 710021, P.R. China
E-mail: licuiyan@sust.edu.cn

Abstract. Bamboo slices have been pyrolyzed by heat treatment in an inert atmosphere at 1000°C. The reaction of gaseous SiO and pyrolyzed bamboo slices at 1300°C resulted in the formation of SiC nanowires. Microstructure characterization of the SiC nanowires was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD analysis showed that the reaction product is crystalline β-SiC. The diameter and the length of the SiC nanowires is ranging from 20~70nm to 10~20μm. Most of the SiC nanowires possess straight and smooth morphology. SiC nanowires have a preferential growth axis parallel to the [111] direction.

1. Introduction
SiC nanowires are very promising because of their large elasticity and strength compare to SiC whiskers or bulk SiC. Such materials can be widely used to reinforce ceramic, metal, and polymer materials [1-4]. In addition, SiC nanowires have great potential for use in electron emitting filaments because of their unique optical and field emitting properties [5, 6]. Therefore, considerable efforts have been devoted to the synthesis of SiC nanowires.

Carbothermal reduction is a useful method for the synthesis of SiC nanowires. Kinds of reductant have been developed for the synthesis of SiC nanowires, such as carbon nanoparticles, carbon nanotubes (CNTs) and amorphous activated carbon (AAC) [6-8]. However, these reductants have some disadvantages which may limit the synthesis and application of SiC nanowires. It may cause quantity of SiC particles mixed in the products by fabrication of SiC nanowires from carbon nanoparticles or amorphous activated carbon. Employing the CNTs as templates in the formation of SiC nanowires can obtain high purity nanowires, but the cost of CNTs restrain its application.

To overcome these disadvantages, SiC nanowires were synthesized via carbothermal reduction of SiO with the pyrolyzed bamboo slices in our experiment. There are many advantages to apply pyrolyzed bamboo slices for the synthesis of SiC nanowires. Firstly, the pyrolyzed bamboo presents the character of amorphous activated carbon. The large specific surface area of the pyrolyzed bamboo is benefit to the growth of SiC nanowires [9]. Secondly, the pyrolyed bamboo contents the elements Fe, Si and K, which might be catalyst in the synthesis of SiC nanowires [10]. Thirdly, the slices structure of the pyrolyzed bamboo can avoid the formation of the SiC particle in the products, which was generated from the particle AAC. In addition, the growth cycle of bamboo is short, which is considered as renewable forest resources. The cost of raw materials for the synthesis of SiC nanowires is low.
In this work, the SiC nanowires was prepared by the carbothermal reduction of SiO and pyrolyzed bamboo. The morphology of SiC nanowires was characterized by SEM. The microstructure of the nanowires was analyzed by XRD and TEM. The growth mechanism of SiC nanowires was discussed.

2. Experimental

2.1. Preparation of pyrolyzed bamboo slices
Bamboo slices were in dimensions of 80 mm × 10 mm × 3 mm. The specimens were rinsed with water and then dried at 70°C for 24 h. Subsequently, the specimens were pyrolyzed at 1000°C for 10 h in flowing argon atmosphere with slow heating rate of 1°C/min up to 400°C and a higher rate of 5°C/min up to 1000°C.

2.2. Carbothermal reduction
Carbothermal reduction of the gaseous SiO was performed in a vacuum sintering furnace. A graphite crucible, which is 60 mm in diameter and 100 mm in height, was put in the furnace. The graphite crucible was fed with the mixture powder of Si and SiO2 and the pyrolyzed bamboo slices. The slices were inserted in the mixture powder of Si and SiO2. Then the furnace was heated to 1300°C and maintained at this temperature for 1 h under flowing argon atmosphere. Finally, the furnace was naturally cooled to room temperature.

2.3. Characterization of Samples
The phases of the samples were identified by X-ray diffractometer (XRD, Cu-Kα, X’Pert HighScore). The microstructure of the samples was characterized by means of scanning electron microscopy (SEM, JSM-6064) and high resolution transmission electron microscopy (TEM, JEM-2010).

3. Results and Discussion

3.1. Pyrolyzed bamboo slices
After pyrolysis, there is significant volume shrinkage for the bamboo slices. The weight loss was found to be about 70–80 wt% for the samples. The bio-structure of bamboo was still retained, as shown in Figure 1.
3.2. SiC nanowires

Figure 2 (a) presents the XRD diffraction result of the pyrolyzed bamboo slices. The two broad peaks located at 22° and 44° corresponded to (0 0 2) and (1 0 0) peaks of the carbon. It is indicated that the bamboo slices had absolutely converted to charcoal. Figure 2 (b) presents the XRD diffraction result of the pyrolyzed bamboo after carbothermal reduction reaction. The XRD pattern containing peaks at 35.67°, 60.11°, and 71.87° indicated that these β-SiC generated after carbothermal reduction. Apart from these three peaks, one extra shoulder peak located at 33.73° was a characteristic peak indicating typical stacking faults on the (1 1 1) planes in β-SiC.

![Figure 2. XRD patterns of (a) the pyrolyzed bamboo and (b) the pyrolyzed bamboo after carbothermal reduction reaction.](image)

The SEM images of the pyrolyzed bamboo slices after carbothermal reduction reaction are shown in figure 3. It can be seen that a large quantity of SiC nanowires has been obtained on the surface of the pyrolyzed bamboo slices. The SiC nanowires randomly distribute on the surface of the pyrolyzed bamboo slices, as shown in figure 3 (a). Most of the SiC nanowires are straight and smooth, as shown in figure 3 (b). Some of the SiC nanowires were curved and twisted. The diameter and the length of the typically SiC nanowires is ranging from 20~70nm and 10~20μm.

![Figure 3. SEM image of the pyrolyzed bamboo slices after carbothermal reduction reaction.](image)
shown in figure 4 (c). The SAED pattern (inset in figure 4 (c)) exhibited a set of diffraction spots along the (111) zone axis. It is indicated that the striations normal to the axes in figure 4 (c) are stacking faults normal to the [111] direction.

![Figure 4. TEM image of the SiC nanowires.](image)

3.3. Growth Mechanism of SiC Nanowires
In our experiment, a mixture powder of Si/SiO$_2$ was used as the SiO(g) source. SiO(g) was produced from a mixture of Si and SiO$_2$. Generally, the following reactions are considered in the the SiO-C system [3, 9].

\[
\begin{align*}
&\text{Si}_2 + \text{SiO}_2 \rightarrow \text{SiO} \\
&\text{SiO} + \text{C} \rightarrow \text{SiC} + \text{CO} \\
&\text{SiO} + \text{CO} \rightarrow \text{SiC} + \text{CO}_2 \\
&\text{CO}_2 + \text{C} \rightarrow \text{CO}
\end{align*}
\]

First, gaseous SiO react with carbon nanoparticle on the surface of the pyrolyzed bamboo slices, the products are SiC nanograins and gaseous CO; and then, reaction (3) is a gaseous phase reaction between SiO and CO, which can occur under a supersaturated condition of CO vapor. Reactions (3) and (4) have a positive feedback characteristic to each other and lead to a supersaturation of CO vapor ultimately. The SiC nanowires can grow under the supersaturation condition of CO. The SiC nanowires start their growth from SiC nanoparticles, which is serves as a SiC nucleus. The growth direction is along the (111) plane for SiC. Some curved nanowires were found as shown in Fig.4 (b). The growth of curved nanowires is due to the growth direction changes in the growth condition [9].
4. Conclusions
SiC nanowires with 20–70nm diameter and 10–20μm length have been synthesized by a reaction between SiO and pyrolyzed bamboo at 1300°C. Most of the SiC nanowires possess straight and smooth morphology. SiC nanowires has a preferential growth axis parallel to the [111] direction.

Acknowledgment
This work has been supported by the Ph. D. Programs Foundation of Ministry of Education of China under Grant No. 20070708001 and the Natural Science Foundation of Shanxi University of Science & Technology under Grant No.ZX07-15.

Reference
[1] Meng G W, Zhang L D, Mo C M, Zhang S Y, Qin Y, Feng S P and Li H J 1998 J. Mater. Res. 13 2533
[2] Shin Y, Wang C, Samuels W D and Exarhos G J 2007 Mater. Lett. 61 2814
[3] Kholmanov I N, Kharlamov A, Barborini E, Lenardi C, Bassi A L, Bottani C E, Ducati C, Maffi S, Kirillova N V and Milani P 2002 J. Nanosci. Nanotech. 2 1
[4] Li Y B, Xie S S, Zou X P, Tang D S, Liu Z Q, Zhou W Y and Wang G 2001 J. Crys. Grow. 223 125
[5] Gao Y, Bando Y, Sato T and Kitami Y 2001 Jpn. J. Appl. Phys. 40 1065
[6] Wu R B, Yang G Y, Pan Y and Chen J J 2007 J. Mater. Sci. 42 3800
[7] Meng G W, Zhang L D, Qin Y, Mo C M and Phillipp F 1999 NanoStructured Mater. 12 1003
[8] Gundiah G, Madhav G V, Govindaraj A, Seikh M M and Rao C N R 2002 J. Mater. Chem. 12 1606
[9] Gao YH, Bando Y, Kurashma K and Sato T 2002 J. Mater. Sci. 37 2023
[10] Cheung T, and Ng D 2007 J. Am. Ceram. Soc. 90 559