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Preparation of high-quality ß-SiC nanowhiskers by using carbon fibres as carbon source

Y. J. WU, W. QIN, Z. X. YANG, J. S. WU, Y. F. ZHANG*
Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Research Institute for Micro/Nanometer Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, People's Republic of China
E-mail: yfzhang@sjtu.edu.cn

Recently, many novel one-dimensional nanomaterials have been prepared and investigated in detail. Since ß-SiC nanowhiskers are of extremely high hardness, high thermal and chemical stability and possess a wide band gap, they are viewed as promising material in applications from electronic devices to novel composite materials [1–6]. ß-SiC nanowhiskers have been synthesized by various techniques, such as carbon nanotubes confined reaction (CNCR), hot filament chemical vapor deposition (HFCVD), carbothermal reduction, and floating catalyst method [7–10]. In the process of preparing ß-SiC nanowhiskers, the selection of the carbon source is a key factor. Presently, the carbon sources used usually include carbon nanotubes, carbon powders, activated carbon, and C_6H_6. CNCR needs expensive carbon nanotubes as carbon source [7], which is unfavorable to large-scale production. HFCVD [8] and the floating catalyst method [10] use carbon powders and C_6H_6 as carbon source, respectively. Both of these two methods need to employ catalysts, which are difficult to be removed from the final products. Activated carbon used in the carbothermal reduction method easily makes the SiC nanowhisker connect to chains [9]. At present, suitable carbon sources are still under investigation for effectively preparing SiC nanowhiskers. In the present paper we chose cheap carbon fibers with diameters in micrometer scale as the carbon source to react with the mixture of SiO_2 and Si powders to prepare high-quality ß-SiC nanowhiskers. The microstructure of the product is analyzed and a possible formation mechanism is proposed.

The schematic diagram of the SiC nanowhisker preparation apparatus is depicted in Fig. 1. This high-frequency induction heating system is mainly composed of a quartz tube, a high-purity graphite cylinder, and copper induction coil. The high-purity graphite cylinder is placed in the middle of the quartz tube wrapped by the induction coil. Micrometer-scale carbon fibers were packed tightly in the upside of the graphite cylinder and the mixture of SiO_2 and Si powders with molar ratio of 1:1 was placed at the bottom of the graphite cylinder. After pumping down the quartz tube to a pressure of 5.3 Pa, argon gas was flowed through the quartz tube at 100 sccm for keeping 2.7×10^3 Pa inert atmosphere. The reaction was carried out at 1500 °C for 10 min and subsequently cooled to room temperature. The bright-blue SiC nanowhiskers growing on the surfaces of carbon fibers were collected. The SiC nanowhiskers were characterized by X-ray diffraction using Cu K_α radiation (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Fig. 2 is a XRD pattern of synthesized nanowhiskers, which shows several peaks assigned to ß-SiC. The refinement gave the cell constant $a = 0.4358$ nm, which is very close to the reported value for ß-SiC ($a = 0.4359$ nm, JCPDS Card. No. 29-1129). There is a low intensity peak near $2\theta = 33.5°$ marked with ♦. Liang *et al.* [11] confirmed that this peak results from the stacking faults, which is attributed to the relative shift between the blocks of atomic layers in the process of growth of ß-SiC nanowhiskers [9, 11–14]. Other diffraction peaks are hardly observed in Fig. 2, indicating the purity of ß-SiC nanowhiskers prepared by the present method is rather high.

Fig. 3a shows the original carbon fibers. These carbon fibers have 15–20 μm diameter and a smooth surface, and are used as the provider of carbon species in the preparation of SiC nanowhiskers. Fig. 3b is a low-magnification SEM image of the as-prepared ß-SiC nanowhiskers growing evenly on the surface of a carbon fiber. It can be seen that there exists a thick ß-SiC nanowhisker layer, like floc, wrapped around the surface of the carbon fiber, with a thickness of about 10–20 μm. Compared with Fig. 3a, the surface of the carbon fiber in Fig. 3b seems very coarse. This indicates that carbon loss occurred to carbon fibers in the reaction process and carbon species in ß-SiC nanowhiskers are provided from the carbon atoms on the surface of the carbon fibers.

A high-magnification TEM image of the ß-SiC nanowhikers is shown in Fig. 4. It can be seen that most of the product exhibits wire-like structure and the whiskers are of uniform diameter ranging from 10 to 40 nm, with length up to a micrometer. Other products, such as carbon powders, amorphous carbons and chains connected by SiC nanowhiskers are not found among the final products. This shows that the present method

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*Author to whom all correspondence should be addressed.

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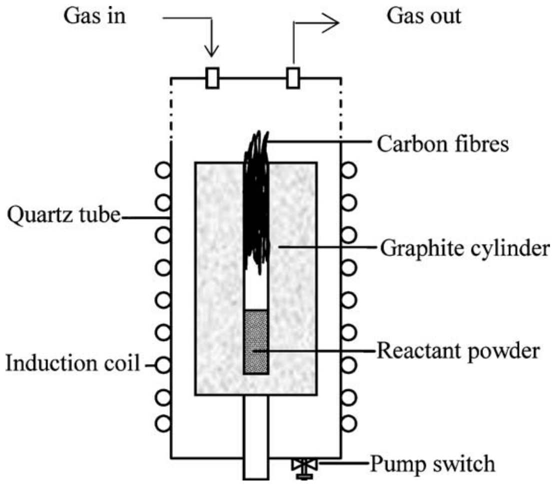

Figure 1 Schematic drawing describing reactor system.

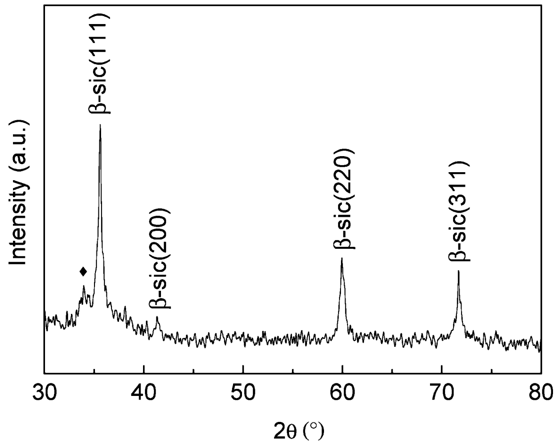

Figure 2 XRD pattern of the as-prepared product.

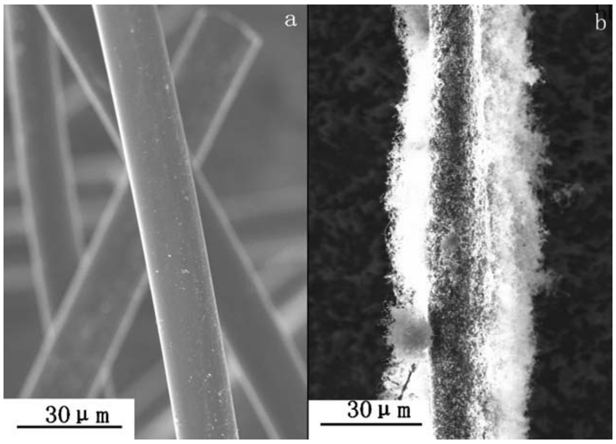

Figure 3 A SEM image of carbon fibers used to be carbon source (a) and a SEM image showing as-prepared ß-SiC nanowhiskers growing on the surface of a carbon fiber (b).

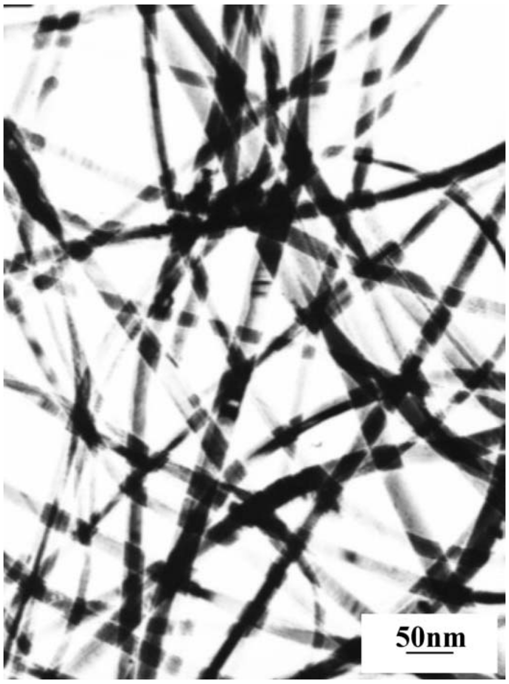

Figure 4 A TEM image of the ß-SiC nanowhiskers.

is superior to HFCVD, carbothermal reduction method and the floating catalyst method.

We suggest that the growth of SiC in our work is an epitaxial growth of ß-SiC nanowhiskers on some random spots of the surfaces of carbon fibers, as indicated in Fig. 3b. The formation mechanism of ß-SiC nanowhiskers in the present method is proposed as follows. As the furnace was heated to 1500 °C, the siliconthermal reaction will take place

$$\mathrm{Si}\,(l) + \mathrm{SiO_2}\,(l) \rightarrow 2\mathrm{SiO}\,(g) \tag{1}$$

where l and g refer to the liquid state and the gas state, respectively. The melting points of Si and SiO_2 are 1412 °C and 1450 °C, respectively, and Equation 1 represents a liquid-liquid reaction. Since the heating system in the present work is high-frequency induction heating and a graphite cylinder is used as the container of the reaction, the heating speed will be very rapid. In addition, in the reaction process, the upside of the graphite cylinder was tightly stuffed with carbon fibers. Therefore, the partial pressure of gaseous SiO produced in the graphite cylinder will be very high. When the gaseous SiO meets with the activated carbon atoms on the surfaces of carbon fibers, SiC nanoparticles may be formed by the reaction

$$\mathrm{SiO}\,(g) + 2\mathrm{C} \rightarrow \mathrm{SiC}\,(\text{nuclei}) + \mathrm{CO}\,(g) \tag{2}$$

These SiC nanoparticles may serve as the SiC nuclei for further growth of straight SiC nanowhiskers. In the process of SiC nanowhisker growth, Si and C species may be further provided via the following reaction

$$\mathrm{SiO}\,(g) + \mathrm{CO}\,(g) \rightarrow \mathrm{SiC}(\text{nanowhisker}) + \mathrm{CO_2}\,(g) \tag{3}$$

The CO_2 vapor generated can further partake in the following reaction

$$\mathrm{CO_2}\,(g) + \mathrm{C}\,(s) \rightarrow \mathrm{CO}\,(g) \tag{4}$$

From reactions (2–4), it is seen that the product of CO vapor is of a positive feedback characteristic. A condition of supersaturation of CO vapor will be formed. According to a kinetic growth mechanism proposed in Ref. [9], with the help of a supersaturation of CO vapor, the SiC nanowhiskers may grow along a fixed axis. A similar growth kinetic mechanism has been also described in our former works [15].

The carbothermal reduction method, using amorphous carbon as carbon resource, needs a long reaction time [9]. HFCVD and the floating catalyst method needs ferrocene [8] and iron particles [10] as catalyst, respectively. So far, there is no literature on using carbon fibers as the carbon resource for preparing SiC nanowhiskers with no help of the catalyst. In the present work, we observed that SiC nanowhiskers easily grow on the surfaces of carbon fibers without catalyst in a few minutes. The reason would stem from two aspects: (a) the reaction temperature in our experiments can be rapidly heated up toward 1500 °C, which is higher than that in the carbothermal reduction method (1380 °C) [9], the floating catalyst method (1200 °C) [10] and HFCVD (1100 °C) [8]. Such high reaction temperature will make the atoms on the surfaces of carbon fibers become more active. (b) CO vapor and SiO vapor produced in the reaction process are limited in the graphite cylinder. Therefore, they will reach very high partial pressure in a short time. These two factors would be the reason why the ß-SiC nanowhikers can be formed rapidly on the surface of carbon fibers.

In conclusion, SiC nanowhiskers with 10–40 nm diameter and micrometer-scale length have been successfully prepared by using carbon fibre as carbon source at 1500 °C reaction temperature without catalyst. It is believed that the elevation of the reaction temperature and the increase of the partial pressures of SiO vapor and CO vapor are the key factors resulting in the production of a mass of β-SiC nanowhiskers on the surfaces of the carbon fibers. Our method could make it possible to produce high-quality β-SiC nanowhiskers at a low cost and on a large scale.

Acknowledgments

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