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Synthesis of hexagonal prism-shaped SiC nanowires from a mixture of bamboo flour and silica xerogel

ZHONG LI*, YUANYUAN QIAN, JIA ZHAO, TONNGHE YAO, DEXIN TAN, MINGGONG CHEN
School of Chemical Engineering, Anhui University of Science & Technology, Huainan 232001, China

Large-scale SiC nanowires with hexagonal prism-shaped have been successfully synthesized by the carbothermal reduction without catalyst assistant. In the process, a mixture of bamboo flour and silica xerogel was chosen as raw materials. The phase composition, morphology and microstructure were investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM). The results showed that the nanowires were grown as single crystalline 3C-SiC along the [111] direction and have diameters of 100-200 nm with lengths up to several tens of micrometers. The growth of SiC nanowires is governed by vapor-solid(VS) mechanism.

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1. Introduction

Over the past decade, much effort has been devoted to the preparation and characterization of one-dimensional (1D) nanomaterials, due to their extraordinary physical properties and extensive potential applications in nanoscale devices [1, 2]. So far, several types of 1D nanomaterials with different compositions have been successfully synthesized, such as SiC [3], ZnO [4], GaN [5] and TiO_2 [6]. Among them, 1D SiC nanostructure, as an important semiconductor and ceramic material, are especially of interest for its outstanding properties of high mechanical strength, high thermal and chemical stability, wide band gap, unique optical property and good field-emitting performance [7, 8].

It is well known that the properties and applications of nanomaterials are strongly influenced by their shape. To date, 1D SiC nanostructures with various shapes such as springs [9], belts [10], wires [11], tubes [12] and beaded nanochains [13], have been synthesized by some methods including laser ablation, arc-discharge, chemical vapor deposition, carbothermal reduction and carbon nanotube-converted reaction and so on [14-18]. However, expensive chemicals, special equipments and strict processing conditions are required in most of these methods. A simpler and more effective approach to prepare single crystalline SiC nanowires is highly desired.

In the present study, large-scale hexagonal prism-shaped SiC nanowires were synthesized by the carbothermal reduction without catalyst assistant. A mixture of bamboo flour and silica xerogel was chosen as the starting materials. This process has inherent advantages, including the availability of low cost raw materials and the simplicity of the production procedures. The morphologies and crystal structures of SiC nanowires were characterized and investigated in detail.

2. Experimental

2.1 Material preparation

All the reagents used in this research are analytical grade. The synthesis process included a mixture of bamboo flour and silica xerogel preparation and subsequent carbothermal reduction. 8.0 g of bamboo flour (with particle size about 200 mm, Anhui, China) was added to a silica precursor solution (total 60 mL, tetraethoxysilane, ethanol and H_2O in the molar ratio of 1:4:4) with stirring. The mixture was then transferred into a self-made sealed infiltration vessel (with a filling ratio of 80%). The vessel was closed and heated in an oven at 120 ^oC for 24 h. Finally the gel was dried in air at 110 ^oC for 12 h to obtain a mixture of bamboo flour and silica xerogel.

The carbothermal reduction was carried out in a horizontally tubular furnace. The mixture in an alumina boat was sent to the heating zone of the furnace. Afterward the furnace temperature was initially raised to 1000 ^oC at a heating rate of 10 $^oC/min$ in argon (>99.99%) flowing atmosphere, then heating continued at 2 $^oC/min$ to a temperature of 1450 ^oC which was maintained further for 4 h. After cooling to room temperature, a large yield of grayish cotton-like products was deposited on the surface of the bamboo flour and silica xerogel mixture. The samples were collected by mechanical separation method.

2.2 Characterization

Field emission scanning electron microscopy (FESEM, FEI, Sirion-200) equipped with energy-dispersive X-ray (EDX) spectroscopy, high resolution transmission electron microscope (HRTEM, JEOL, JEM-2010), Fourier transform infrared spectroscopy (FT-IR, PE, Spectrum-100) and X-ray diffraction (XRD, D/max-2200, Rigaku were employed to characterize the as-synthesized products. The samples for FESEM were presputtered with a conducting layer of Au for 1 min at 10 kV.

3. Results and discussion

Phase identification of the grayish as-synthesized products was characterized using the XRD pattern. The typical XRD pattern shown in Fig. 1 indicates that the intensive characteristic peaks located at 2θ = 35.7, 41.5, 60.1, 71.9 and 75.5^o can be ascribed to (111), (200), (220), (311) and (222) diffractions of cubic 3C-SiC, respectively. The lattice parameter calculated based on the d spacing of each diffraction peak is 0.4356 nm, which is in good agreement with the value of a =0.4359 nm reported in JCPDS 29-1129. These sharp diffraction peaks indicate that the products are highly crystalline. Moreover, the stronger (111) diffraction peak indicates that the [111] is the dominant growth direction of the SiC nanowires.

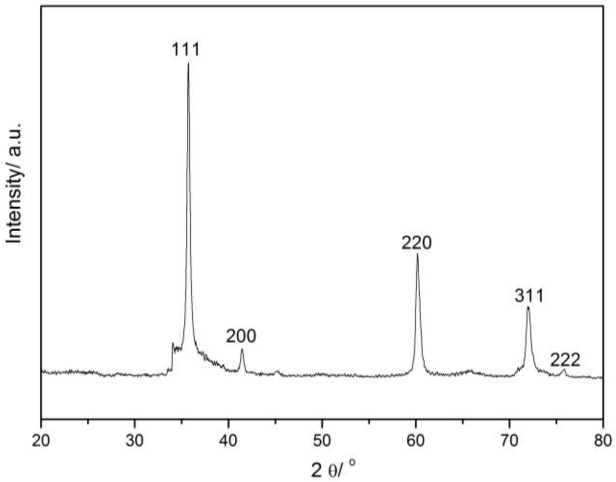


Fig. 1. XRD pattern of the as-synthesized SiC nanowires.

The FT-IR spectrum of the products is shown in Fig. 2. A strong absorption band at 798 cm^{-1} is ascribed to the C-Si stretching vibration mode in the SiC crystalline phase [19].

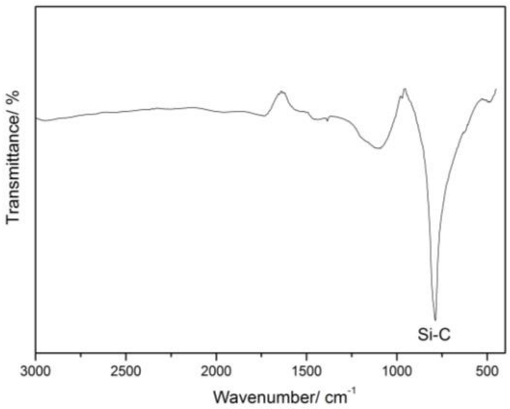
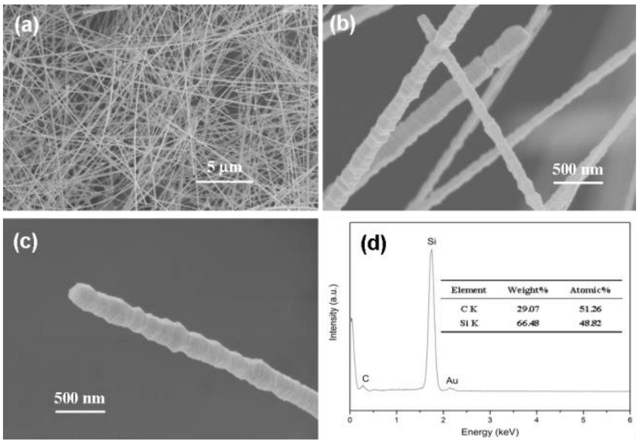


Fig. 2. FT-IR transmittance spectrum of the as-synthesized SiC nanowires.

FESEM examination was conducted to investigate the morphology characteristics of as-synthesized products. Fig. 3 shows a set of the images at different magnifications. Fig. 3a gives an overall view of the sample, showing that there are large-scale SiC nanowires with high density. The nanowires shown in Fig. 2b are straight and clean without impurity. The diameters and lengths of the nanowires are about 100–200 nm and up to tens of micrometers, respectively. The magnified FESEM image, Fig. 3c, further indicates the nanowires are hexagonal prism-shaped with flat tip. Moreover, the nanowires consist of many small parallel platelet-like segments, which appear alternately along the growth axis and vary slightly in diameters, and therefore result in rough lateral surface of the nanowire. Elemental analyses by EDX (Fig. 3d) indicate that the as-synthesized nanowire is composed of Si and C elements and the corresponding atomic ratio is close to 1:1(Au element coming from the conducting layer of Au).



Element	Weight%	Atomic%
C K	29.07	51.26
Si K	66.48	48.82

Fig. 3. Morphology and chemical composition of the as-synthesized nanowires. (a) Low-magnification FESEM image of SiC nanowires. (b) High-magnification FESEM image of some SiC nanowires. (c) FESEM image of one of SiC nanowire with a hexagonal cross section. (d) EDX spectra of the surface of the SiC nanowire.

The morphological details of the hexagonal prism-shaped SiC nanowires are highlighted in TEM images (Fig. 4). Fig. 4a shows the morphology of a representative nanowire with the stacked hexagonal crystalline platelets along their growth direction and the rough lateral surface. Fig. 4b, 4c are an HRTEM image of the nanowire, in which numerous stacking faults or microtwins can be seen. The spaces between two adjacent lattice fringes are 0.25 nm corresponding well to the (111) planes of 3C-SiC. The (111) fringes are perpendicular to the nanowire axis, indicating that the SiC nanowire grew along the [111] direction. The corresponding SAED pattern (inset of Fig. 4b, 4c) obtained from HRTEM can also be indexed to 3C-SiC structure and confirms the XRD result presented above.

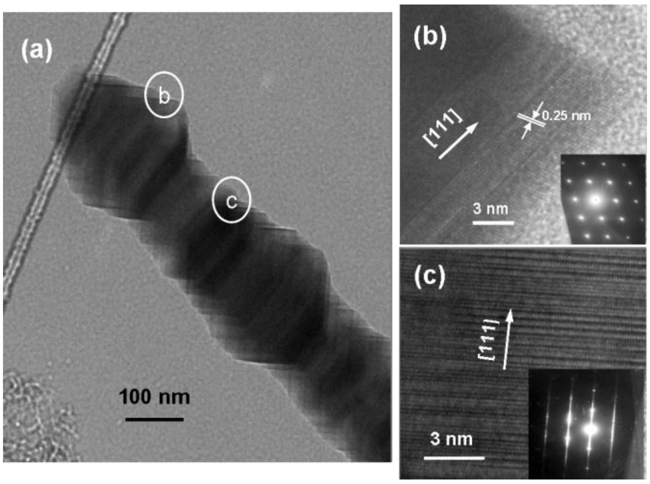


Fig. 4. (a) Typical TEM image of the hexagonal-shaped SiC nanowire. (b, c) Coressponding HRTEM image of nanowire with defects and Corresponding selected area electron diffraction pattern (inset).

Based on the above-mentioned experimental results, we proposed a possible growth mechanism for the hexagonal prism-shaped SiC nanowires. The two widely accepted SiC nanowires growth mechanisms are vapor-liquid-solid (VLS) and vapor-solid (VS) mechanisms. In this work, no catalyst was introduced and no additional metal droplets were detected at the tips of the nanowires from FESEM and TEM images (Fig. 3 and Fig. 4), which is a critical feature of the metal-catalyst VLS mechanism [20, 21]. Therefore, the VS mechanism might be employed to explain the formation process of the SiC nanowires.

When the temperature rose gradually, the bamboo flour in the raw materials were firstly pyrolyzed in situ to form biocarbon (C). Then, SiO_2 component is reduced by C to generate gaseous SiO and CO according to reaction (1):

$$SiO_2(s,l) + 3C(s) \rightarrow SiC(s) + 2CO(g) \tag{1}$$

where *s*, *l*, and *g* refer to the solid state, the liquid state and the gas state, respectively. Subsequently, the reactions (2) and (3) can take place simultaneously.

$$SiO_2(s) + CO(g) \rightarrow SiO(g) + CO_2(g) \tag{2}$$

$$CO_2(g) + C(s) \rightarrow 2CO(g) \tag{3}$$

As the reactions proceeded, the gaseous SiO molecule reacts with its surrounding C and forms SiC nuclei heterogeneously on the surfaces of biocarbon, which can be expressed as:

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \tag{4}$$

To maintain the lowest surface energy and the lowest specific line tension, a generated SiC nucleus would have a two-dimensional hexagonal shape with a (111) plane and six (110) peripheral planes. The peripheral plane should be the preferential place for the SiC nuclear to grow in radial direction and the radial growth still relied on reaction (4) because it takes place on the surfaces of biocarbon and involves a short distance diffusion of carbon atoms [22]. The nucleation stage for the growth of anisotropic shapes determines the shape of the resulting nanowires.

As soon as SiC forms on biocarbon, the growth process via reaction (4) could be hindered by either the solid diffusion of carbon or the diffusion of SiO gas molecules through SiC [23]. On the other hand, the continuous generation of CO and SiO leads to supersaturation. As the SiO and CO diffused to the surface of nuclei, SiC nanowires could grow through gas-gas reaction according to reaction (5).

$$SiO(g) + 3CO(g) \rightarrow SiC(s) + 2CO_2(g) \tag{5}$$

Because of reasons based upon the lowest energy principle, it is generally accepted that the 3C-SiC nanowires should grow preferentially along the [111] direction, and the stacking faults can be inserted in the (111) planes to decrease the formation energy [24]. With the prolonging of the reaction time, hexagonal prism-shaped SiC nanowire with rough lateral surface, which also results from maintaining the minimum surface energy, is formed. The HRTEM investigation shown in Fig. 4 confirms this argument. However, the influence of the ratio of thickness to length is still unclear, and further work is needed for a full understanding. In the present work, the interconnected porous structures from bamboo flour after initial carbothermal reduction could facilitate the diffusion of the reactant gaseous SiO, CO, and CO_2, which is helpful to improve the yield of SiC nanowires.

4. Conclusion

Large-scale hexagonal prism-shaped SiC nanowires have been successfully synthesized by a simple catalyst free carbothermal reduction from a mixture of bamboo flour and silica xerogel. The nanowires formed through the VS mechanism, and had diameters of 100-200 nm and lengths up to several tens of micrometers. A typical SiC nanowire is composed of uniform 3C-SiC oriented in the (111) direction and stacking faults perpendicular to [111] plane. The special shape SiC nanowires are expected to build novel electronic devices and the rough lateral surfaces are considered to improve the mechanical properties of SiC-reinforced composite materials. It is noteworthy that this is a simple and economical process for the synthesis of high yield 3C-SiC nanowires without catalyst.

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* Corresponding author: zhongli-91@163.com