Inverted SiC nanoneeds grown on carbon fibers by a two-crucible method without catalyst

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Inverted single crystalline SiC nanoneeds with hexagonal cross-sections were grown on the surface of carbon fibers by high-frequency induction heating two-crucibles without using any catalysts. we employ a carbothermal reduction method of silicon monoxide with coke fibers to synthesize SiC nanoneeds within 5 min. The as-grown SiC nanoneeds shows bright blue color on carbon fibers in the [1 1 1] orientation of 3C-SiC structure. The needle-like structures grew on the substrate while the spindle portion was sticked into the carbon fibers which were different from other nanoneeds. Finally, the growth mechanism of SiC nanoneeds is proposed to be an axial direction growth with a driving force of screw dislocation and a radial direction growth with vapor–solid mechanism meanwhile.

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1. Introduction

Over the past decade, one-dimensional nanostructure semiconductors, such as silicon carbide nanowires, silicon nanowires, zinc oxide nanowires, gallium nitride nanowires, carbon nanotubes, and so on [1–7], have drawn much attention because of their excellent electrical, optical, and mechanical properties compared to those of their bulk counterparts.

Among them, nanostructure silicon carbide (SiC) is one of the most promising materials due to its excellent properties such as high mechanical strength, high thermal conductivity, high chemical stability [8], and its broad application as reinforcement materials in the fabrication of metal and ceramic matrix composites. In addition, SiC is a new generation of semiconductor with a wide band gap (2.4 eV for 3C-SiC, 3.0 eV for 6H-SiC, and 3.2 eV for 4H-SiC) [9]. Because of its superior properties mentioned above, one dimensional (1D) nanosized SiC has wide potential applications in nanoscale devices used in harsh environments with high frequency and high temperature [10].

In experiments, various types of one dimension (1D) SiC nanomaterials, i.e., nanowires, nanofibers, nanorods, nanotubes, nanocables, and needle-shaped nanowires were synthetized via different approaches. Since the first synthesis of carbide nanorods using carbon nanotube as templates by Dai group in 1995 [11], many approaches have been developed to synthesize 1-D SiC nanostructures. Zhou et al. [12] synthesized SiC nanorods through the conventional carbothermal reduction of electrospin SiO2: Tb nanofibers. Yang et al. [13] grew SiC nanowires and nanorods by simply heating Fe–Si melt on a graphite plate in argon atmosphere to 1600 °C for 3 and 6 h, respectively. Chiu et al. [14] prepared high-purity SiC nanowires through a catalyst-free arc-discharge process with silicon dioxide powders as a filler in a graphite anode. Guozhen et al. [15] obtained single-crystalline bamboo-like beta-SiC nanowires with hexagonal cross-sections by thermal evaporation of mixed SiO and C with GaN powders in Ar atmosphere. Wu et al. [16] synthesized bunches of needle-shaped silicon carbide nanowires from commercially available SiC powders with iron as catalyst in thermal evaporation process. However, very few cases have been reported about rapid synthesis of needle-like SiC nanostructure without any catalysts. This sort of straight SiC nanoneeds may have practical applications in blue and ultraviolet light emitters, field electron emission, reinforced composites, sensors, etc.

In this paper, we report a simple thermal evaporation approach to rapidly synthesize silicon carbide nanoneeds with perfect hexagonal cross-sections, which can provide a further understanding of the growth mechanism of one dimensional SiC nanostructures. The needle-like structures grew on the substrate
invertedly, and the spindle portion was sticked into the carbon fibers which was different from other nanoneedles. In this method, we design a sample device with two home-manufactured hollow cylindrical graphite crucibles to sustain an environment which makes sure both the mixed reactant and substrate can be heated from room temperature to required temperature rapidly. The carbon fibers act not only as substrate but also as reactant in nucleation process, and the mixed reactant in high temperature provide sufficient gas source for side direction growth, which results in needle-like nanostructure. In addition, it exhibits a growth mechanism different from the traditional V–S models or screw dislocations mechanism. A combined mechanism was supposed to interpret the growth of needle-like nanostructure.

2. Experimental detail

2.1. Preparation of SiC nanoneedles

The experiments were performed in a horizontally set high-frequency induction heating furnace as schematically outlined in Fig. 1, which employed two home-made hollow cylindrical graphite crucible with different diameters (A: 22 mm in inner diameter, 30 mm in outer diameter; B: 40 mm in inner diameter, 50 mm in outer diameter). Crucible A contained silicon monoxide (1.1 g) and carbon coke (0.3 g), and Crucible B contained some carbon fibers as substrate. The two graphite crucibles were neighboring each other. The two-crucible set was then moved to a suitable place in a horizontal quartz tube. Deserve to be mentioned, the relative position between the two-crucible set and induction coil can be adjusted to control the temperature field in the two-crucible set roughly. Before heating, the furnace was evacuated to the pressure of about 100 Pa by a rotary mechanical pump. Then high purity argon gas was introduced at a constant rate of 200 sccm and kept the pressure of about 50 kPa until the experiment finished. Afterwards, the furnace was rapidly heated from room temperature to about 1800 °C within 2 min and the temperature was maintained for 5 min, then the furnace was cooled down to room temperature by simply turning the power off.

2.2. Sample characterizations

After the furnace was completely cooled, a large of bluish green product coated on the carbon fibers surfaces was obtained. The morphology and microstructure of the synthetic product were characterized using scanning electron microscopy (SEM, Carl Zeiss, Ultra 55, Germany) and transmission electron microscopy (TEM, JEM-2100, JEOL). The chemical composition of the synthetics was analyzed by the energy dispersive X-rays spectroscopy (EDS, Oxford Instruments INCA PentaFET 3, Model: 7426) equipped on the SEM. The crystal structure of the samples was analyzed using X-ray diffraction (XRD, D/max—2200/PC, Rigaku), which was equipped with a Cu Kα radiation source.

3. Results and discussion

3.1. Structure and morphology

XRD patterns are taken to examine the crystal structure of the obtained products. Fig. 2 shows a typical XRD pattern. Four major diffraction peaks at 35.7°, 41.4°, 60.0°, and 71.8° can be indexed as the (1 1 1), (2 0 0), (2 2 0), and (3 1 1), respectively, which indicates a 3C-SiC structure (JCPDS card no. 29-1129). The lattice parameter of 3C-SiC cubic cell of the sample calculated from the XRD data is \( a = 4.358 \, \text{Å} \), which is in good consistency with the standard value (\( a = 4.359 \, \text{Å} \)). Moreover, the peak marked with A is due to stacking faults according to previous researchers [17,18] and the diffraction peak bulge marked with B between 20° and 30° is the characteristic amorphous carbon peak from carbon fibers.

Surface morphology can be observed from SEM images. Fig. 3(a) presents a typical low magnification SEM image. It can be seen that the products consists of needle-like structures with lengths up to several ten micrometers encircled by some ultrafine
nanowires. The images reveal that these needle-like nanostructures have a spindle portion and a thick portion. From the yellow circles marked in Fig. 3(a) and the enlarged image of a circle (inset in Fig. 3(a)), it is obviously shown that the needle-like structures randomly grew on the substrate, and the spindle portion is stuck into the carbon fibers which is different from other nanoneedles [19]. In order to show a clearer insight into the needle-like nanostructures, high magnification SEM images of several SiC nanoneedles are given in Fig. 3(b). Fig. 3(b) and insets show typical two portions of a SiC nanoneedle, which reveals that the nanoneedle has a smooth surface, and hexagonal cross-sections perpendicular to the growth direction. Shown in Fig. 3(c) is a detailed image of the thick portion. The axial screw dislocation spiral at the tip of the nanoneedle can be seen indistinctly which is driven by screw dislocations mechanism [20,21]. Moreover, the nanoneedle has a perfect hexagonal cross-section, and the intersection angle between two sides is almost 120° and the length of each side is about 130 nm.

SEM and EDS measurements are employed to investigate the carbon fibers after reaction, as a comparison, the same measurements are used in original carbon fibers. Fig. 4(a) shows a SEM image of single original carbon fibers (OCF), revealing that the carbon fibers possesses a smooth surface. The inset image in Fig. 4(a) indicates that the OCF consists of C element and small quantities of O element which may come from the residual gas in the chamber. Fig. 4(b) shows a SEM image of carbon fibers after reaction (RCF), revealing that the carbon fibers possesses a coarse surface with many pores and particles. The inset image in Fig. 4(b) indicates that the RCF mainly consists of C element, Si element, and the atomic ratio of C element and Si element is about 7:2. We further found some delicate differences between OCF and RCF in diameter: the diameters of OCF and RCF are 7.4 ± 0.3 and 7.0 ± 0.3 μm, respectively. This increase in the roughness and decrease in diameter may be attributable to the fact that the carbon fibers act not only as substrate but also as reactant; some gas may generate in carbon fibers during the reaction, which causes coarse surface with many pores and particles.

TEM measurements are employed to investigate the microstructure of the as-prepared SiC nanoneedles. Fig. 5 shows a typical low-magnification TEM image of the prepared SiC nanoneedles, revealing the representative needle morphology, and the
As the temperature is up to 1800 °C, SiO powder will vaporize and react with the carbon source as follows:

\[
\text{SiO(g)} + 2\text{C(s)} \rightarrow \text{SiC(s)} + \text{CO(g)}
\]  

(1)

It will generate CO gas in this process, which provides CO source for next reaction.

\[
\text{SiO(g)} + 3\text{CO(g)} \rightarrow \text{SiC(s)} + \text{CO}_2(g)
\]  

(2)

Silicon may also be formed according to the two following reactions when a large excess of SiO exists compared to CO [28].

\[
\text{SiO(g)} = \text{Si(s)} + \text{SiO}_2(s)
\]  

(3)

\[
\text{SiC(s)} + \text{SiO(g)} \rightarrow 2\text{Si(s)} + \text{CO(g)}
\]  

(4)

At the same time, the CO \(_2\) gas generated from Reaction 2 may react with the carbon source as follows:

\[
\text{CO}_2(g) + \text{C(s)} = 2\text{CO(g)}
\]  

(5)

According to thermodynamics, the Gibbs-free energy \(\Delta G(T)\) of reactions above all is given in Fig. 6 (the thermodynamic data are obtained from software HSC chemistry 5.0). It can be seen that the Gibbs-free energy \(\Delta G(T)\) of the Reaction 1 is always negative, which indicates the reaction between SiO and C can take place. There are two kinds of carbon sources in our experiment, carbon coke in Crucible A and carbon fibers in Crucible B, respectively. In Crucible A, SiO react with carbon particles as follows:

\[
\text{SiO(vapor, liquid)} + 2\text{C(carbon particles)} \rightarrow \text{SiC(solid)} + \text{CO(vapor)}
\]  

(1-1)

This reaction also occurs on the surface of the carbon fibers in-situ. At a high temperature, solid SiO is evaporated to generate SiO gas, and then the SiO gas are transported to the Crucible B and absorbed on the surface of carbon fibers. At the same time, the
carbon on carbon fibers begins to react with SiO to form SiC embryos as the first stage and continue to grow just like bottom-up way. Moreover, attention to the axial screw dislocation spiral at the tip of the nanoneedle in Fig. 3 (c), we can confirm that screw dislocation growth mechanism plays a certain role in forming of SiC nanoneedles. In fact, Reaction 2 can also generate SiC. However, it is noticed that the carbon fibers become coarse with many holes and particles, and decrease in diameter. Therefore, the reaction 1 is considered to be mainly responsible for the nucleation process instead of Reaction 2.

However, screw dislocation growth mechanism cannot explain the inverted needle-like nanostructure completely. The Reaction 2 may explain the growth of inverted needle-like SiC nanostructure. However, Reaction 2 cannot take place in high temperature in thermodynamics. Fortunately, there are sufficient SiO gas and CO gas. Reactions 1 and 4 can provide CO gas source at the temperature in thermodynamics. Fortunately, there are sufficient SiO gas and CO gas. Reactions 1 and 4 can provide CO gas source meanwhile. The screw dislocation growth mechanism results in axial direction growth, and generate nanorods with screw dislocation spiral. It is worth noting that inverted SiC nanoneedles can not be formed just by screw dislocation growth mechanism. Therefore, vapor–solid mechanism is performed on the surface of nanorods at the same time, and results in side direction growth. The earlier out of the as-grown nanorods, the more time reaction by vapor–gas mechanism, and finally generate inverted SiC nanoneedles.

4. Conclusion

In conclusion, single crystalline needle-like SiC without amorphous layer were synthesized rapidly by a high-frequency induction of two-crucible method. The SiC nanoneedles with 3C-SiC structure, possess perfect hexagonal cross-sections, and grow along the [1 1 1] direction. The carbon fibers after reaction possess a coarse surface with many pores and particles, and decrease in diameter obviously. The growth process of the SiC nanoneedles start from the initial SiC nuclei forming in the reaction process between SiO gas and carbon on the surface of carbon fibers, then grow along the [1 1 1] direction which is proposed to be dominated by screw dislocation effect, at the same time a side direction growth controlled by vapor–solid mechanism, and finally generate inverted SiC nanoneedles.

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