Nanoscale Res Lett (2009) 4:153–156
DOI 10.1007/s11671-008-9216-3

NANO EXPRESS

SiC Nanowires Synthesized by Rapidly Heating a Mixture of SiO and Arc-Discharge Plasma Pretreated Carbon Black

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Received: 17 September 2008 / Accepted: 11 November 2008 / Published online: 22 November 2008
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Abstract SiC nanowires have been synthesized at 1,600 °C by using a simple and low-cost method in a high-frequency induction furnace. The commercial SiO powder and the arc-discharge plasma pretreated carbon black were mixed and used as the source materials. The heating-up and reaction time is less than half an hour. It was found that most of the nanowires have core-shell SiC/SiO_2 nanostructures. The nucleation, precipitation, and growth processes were discussed in terms of the oxide-assisted cluster-solid mechanism.

Keywords Silicon carbide · Nanowires · Induction heating

Introduction

Silicon carbide (SiC) has been widely used in the fields of electronic and optic devices due to its unique properties, such as a wide band gap of 2.3–3.3 eV, high strength, and Young's modulus, good resistance to oxidation and corrosion, excellent thermal conductivity, and electron mobility [1–4]. One-dimensional (1D) SiC materials, i.e., nanowires, nanofibers, nanorods, and nanocables have recently attracted much attention because they have been thought suitable for the fabrication of high temperature, high frequency, and high power nanoscaled electronic devices [5–9].

The first successfully synthesis of 1D SiC nanowires was in 1995 by using carbon nanotube as a template [10]. Up to now, lots of approaches have been developed, for example, arc-discharge [11], laser ablation [12], sol–gel method [13], carbon thermal reduction [14], and chemical vapor deposition [15]. Recently, metal catalyst assisted synthesis of 1D SiC nanostructures had also been reported [16, 17]. In most of these methods, expensive raw materials, catalysts, and sophisticated techniques were used. These drawbacks may limit the massive fabrication and application of SiC nanowires. It is still a challenge for scientists and industrials to synthesize large-scale SiC nanowires by using a simple and rapid method.

In this paper, we report a novel method to fabricate β-SiC nanowires by using a high-frequency induction furnace with a graphite tube. A mixture of commercial SiO and the carbon black powder with loose structures pretreated by an arc-discharge plasma method was used as the starting materials. After heating the source materials in graphite tube in argon atmosphere, bright blue powders can be observed in the tube, which were characterized as β-SiC nanowires with core-shell structures. The total heating-up and reaction time is less than 1 h, and more than 200 g products can obtain per day. The modified oxide-assisted cluster-solid growth mechanism was used to explain the formation of core-shell SiC/SiO_2 nanowires.

Experimental

The fabrication of β-SiC nanowires was carried out in a high-frequency introduction furnace. First, commercial carbon black was pretreated in order to form porous and

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loose structures, which can make the reaction much easier. The carbon black was pressed to a carbon rod and put into an arc-discharge plasma instrument. After treating for about 1 h, a black powder with loose structures was obtained.

The as-prepared carbon black was mixed with the commercial SiO powder (mass ratio of 1:1) and ball-milled for several hours. Then, the precursor was loaded in a graphite boat and located in a high-purity graphite tube. As a heating crucible, the graphite tube was placed in a horizontal quartz tube and heated in a high-frequency induction furnace. The furnace was first evacuated to 50 Pa, and then the argon gas was introduced until the furnace pressure reached about 4×10^4 Pa, which was maintained throughout the whole experimental process. The powder was rapidly heated to 1,600 °C within 3 min and kept for 40 min. A bright blue-colored powder was found in the graphite boat. The schematic diagram of the apparatus is shown in Fig. 1.

An energy-dispersive X-ray (EDX, INCA OXFORD) spectroscopy and an X-ray diffraction (XRD, D/MAX-RA) were used to characterize the composition and crystal structure of samples. A field-emission scanning electron microscopy (SEM, FEI SIRION 200) and a transmission electron microscopy (TEM, JEM-2010) were employed to observe the morphology and the detail structure of the nanowires.

Results and Discussion

Figure 2 shows the typical SEM image of the carbon black, which was treated in an arc-discharge plasma instrument. The loose and porous nanostructures were formed, which have more surface areas compared with original materials. This provides more chance for the reaction with SiO vapor. The inset in Fig. 2 displays the corresponding EDX spectrum, indicating only two elements (carbon and oxide) existed in the pretreated carbon black.

The characteristic XRD pattern of the products is showed in Fig. 3. The major diffraction peaks can be indexed as the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2)

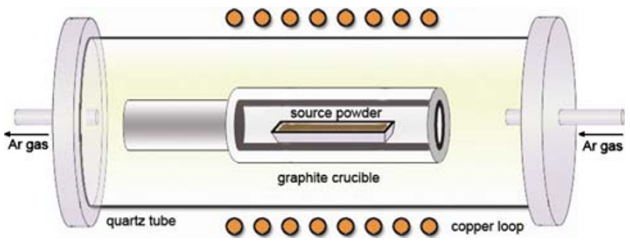

Fig. 1 Schematic diagram of the apparatus for synthesis of SiC nanowires

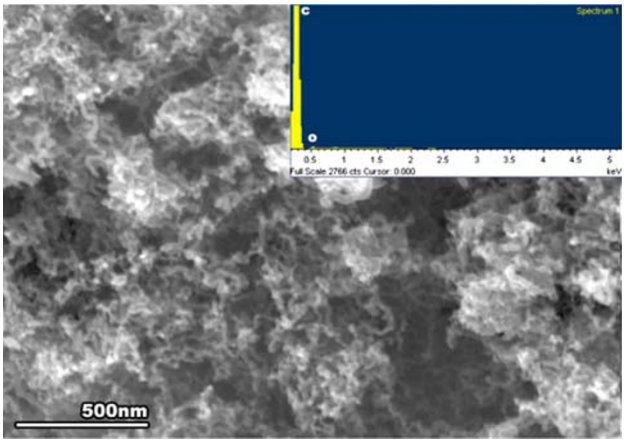

Fig. 2 SEM image and EDX pattern of carbon black after arc-discharge plasma treatment

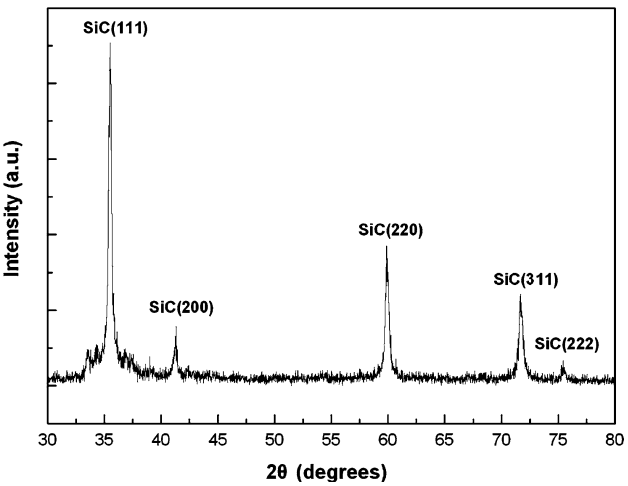

Fig. 3 XRD pattern of the SiC nanowires

reflections of cubic β-SiC (unit cell parameter $a = 0.4370$ nm). These values are almost identical to the known values for standard β-SiC (JCPDS Card No. 29–1129). Moreover, there is amorphous background in the XRD pattern, which is similar to amorphous SiO_2. Furthermore, the diffraction peaks are broadened, which may be related to the inner thinner β-SiC nanowire and the outer amorphous silicon oxide wrapping layer.

Figure 4 shows the SEM and TEM images of the as-synthesized nanowires without any other treatments. In Fig. 4a and b, it can be seen that the nanowires have almost uniform diameters and smooth surfaces. The diameter of nanowires can be roughly estimated in the range of 60–100 nm and the length are several microns. The observed impurities in SEM images were the intermediate product of SiO_2 and the residual carbon. To validate the existing of impurities, high-temperature oxidation and hydrofluoric acid (5%) treatment were used to get rid of the residual carbon and SiO_2, respectively. In the high-temperature

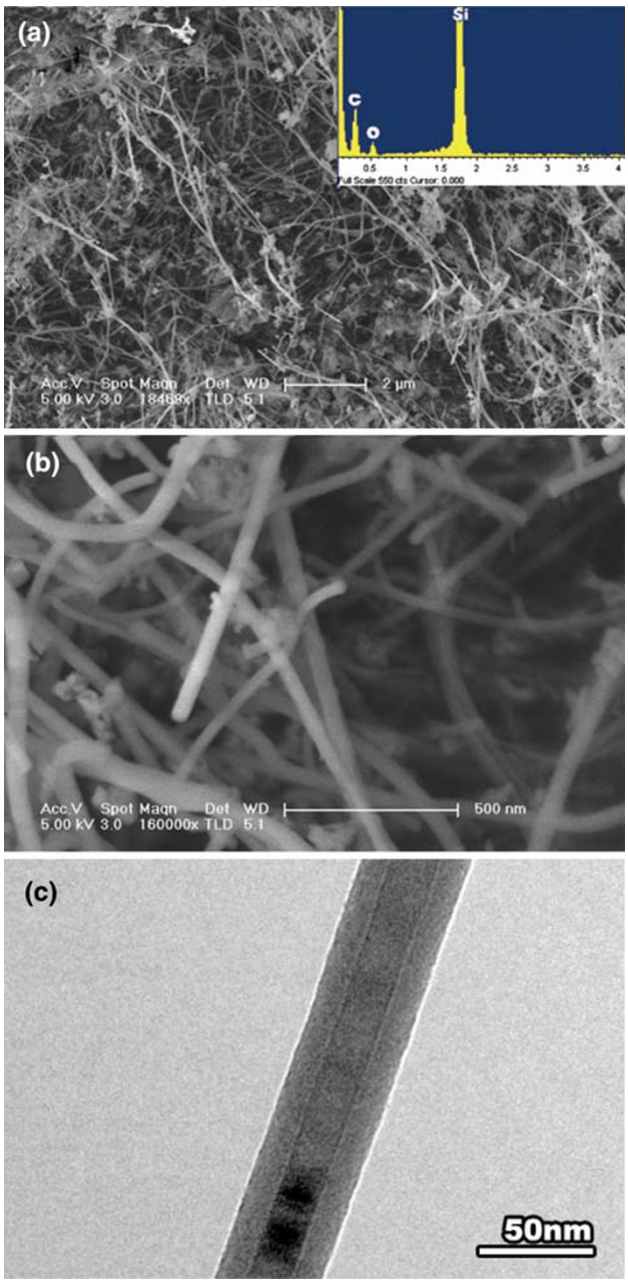

Fig. 4 **a** The SEM image of SiC nanowires; **b** the magnified SEM image of SiC nanowires; and **c** the TEM image of SiC nanwires with a core-shell SiC/SiO_2 structure. The inset in **a** shows the EDX pattern of SiC nanowires

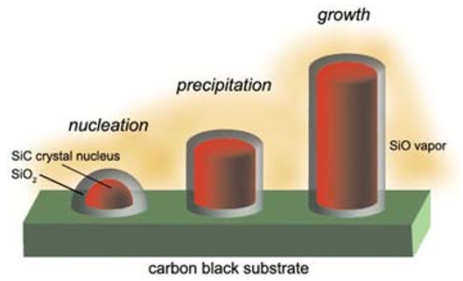

Fig. 5 Schematic diagram of growing process of SiC nanowire

oxidation processing, about 72% of the as-synthesized sample remained as well as 28% of carbon was oxidized. After dipping in hydrofluoric acid (5%) for 2 h, about 74% of the residual sample remained when SiO_2 was corroded. Therefore, it can be concluded that the yield of SiC nanowires was about 53%. The inset in Fig. 4a displays the corresponding EDX spectrum, indicating three elements (silicon, carbon, and oxide) exist in the nanowires. The TEM image in Fig. 4c shows detailed structure of the nanowire. One can find that the nanowire has a core-shell nanocabled structure. According to the component ratio obtained by EDX results, the core ought to be crystallized SiC and the shell is amorphous SiO_2. In fact, the unique core-shell SiC/SiO_2 structure has also been observed by other researchers [18–20].

Vapor–liquid–solid (VLS) mechanism has usually been used to explain the growth process of 1D nanomaterials [21]. However, it seems unsuitable to interpret our experiments and results because there is no catalyst liquid droplet available during the high-frequency induction heating procedure. The oxide-assisted cluster-solid mechanism proposed by Zhang et al. [22], which was established to interpret the growth process of Si/SiO_2 nanowires, may be used to understand the growth process of core-shell SiC/SiO_2 nanowires. In terms of this mechanism, there exist three processes, that is, nucleation, precipitation, and growth. Figure 5 illustrates the schematic diagram of growing process. As the temperature is up to 1,600 °C, SiO powder will vaporize and react with the carbon source as follows:

$$3\mathrm{SiO(v)} + 3\mathrm{C(s)} = 2\mathrm{SiC(s)} + \mathrm{SiO_2(s)} + \mathrm{CO(v)} \quad (1)$$

where v and s refer to vapor and solid states of the material, respectively. It will generate SiC and SiO_2 nanoparticles in this process, which provide crystalline nucleus for growth of nanowires. Actually, three different atoms (silicon, carbon, and oxygen) contained in the nanoparticles. The superfluous of any element will lead to the occurrence of precipitation (separate out) process. Reaction 2 can occur under a supersaturated condition of CO [23]:

$$\mathrm{SiO\ (v) + 3CO\ (v) = SiC\ (s) + 2CO_2\ (v)}. \quad (2)$$

When SiO vapor is prevail, the following reaction will occur:

$$\mathrm{3SiO\ (v) + CO\ (v) = SiC\ (s) + 2SiO_2\ (s)}. \quad (3)$$

No matter what reaction is in the ascendant, SiC can generate and provide to the nanoparticles. Since there exist sufficient silica and carbon atoms in the reaction atmosphere, the precipitation (separate out) of SiC is possible. When the reaction 3 is dominant, SiO_2 is then the

main resultant and can separate out accompanying with the growth of SiC nanocrystals. This is why SiC nanowires are wrapped by SiO_2 layers.

At the same time, the CO_2 gas generated from reaction 2 may react with the carbon source as follows:

$$CO_2(v) + C\ (s) = 2CO\ (v). \quad (4)$$

The partial supersaturation of CO gas can lead to a diameter distribution of the as-synthesized SiC nanowires [24, 25]. The CO gas is hard to be got rid of from graphite crucible in our experiment, and therefore, leads to the distribution of the diameter in as-synthesized SiC/SiO_2 nanowires.

Conclusion

We present a simple, rapid, and low-cost method to synthesize massive β-SiC nanowires by a high-frequency induction heating procedure. A ball-milled mixture of SiO and carbon black was used as source materials. The carbon black were pretreated in an arc-discharge plasma instrument in order to form loose and porous structures. The heating-up and the reaction time is less than 1 h. The nanowires have core-shell SiC/SiO_2 structures in which the core of SiC crystallizes very well, whereas the SiO_2 has amorphous structure. The diameter of nanowires is ranged from 60 to 100 nm and the length is up to several microns. This method provides a promising candidate for industrial fabrication of β-SiC nanowires.

Acknowledgments This work is supported by the National Basic Research Program of China (No. 2006CB300406) and the Shanghai Science and Technology Grant (No: 0752nm015) as well as the National Natural Science Foundation of China (No. 50730008). The authors also thank the Instrumental Analysis Center of Shanghai Jiao Tong University for the Materials Characterization.

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