Synthesis of $\beta$-SiC/SiO$_2$ core-shell nanowires by simple thermal evaporation

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Beta-SiC/SiO$_2$ core-shell nanowires were obtained in a mullite boat after the reaction between silicon nanopowder and CH$_4$ gas at 1623 K (1350°C), without adding metal catalysts from outside. The as-grown nanowires were characterized by X-ray diffractometry, scanning electron microscopy, transmission electron microscopy, scanning TEM, and infrared-ray spectroscopy. The results showed that the typical nanowires consisted of single crystalline $\beta$-phase SiC core of 50–70 nm in diameter and a uniform wrapping layer of low crystallinity SiO$_2$ of ~15 nm in thickness, and their lengths were up to several tens of micrometers. The nanowires axes lay along the [111] direction of $\beta$-SiC. Oxygen from the experimental setup or the raw powder should be a key factor to synthesize the core/shell nanowires.

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1. Introduction

Since the discovery of carbon nanotubes, CNTs, by Iijima in 1991, great attempts have been conducted on the variety of nanoscale structures such as nanowires, nanotubes, nanorods, and nanobelts for their potential applications. Among these nanoscale structures such as nanowires, nanotubes, nanorods, and nanobelts for their potential applications. Extensive activity, high electron mobility, high mechanical strength, large band gap, chemical inertness, and biocompatibility. Both theoretical calculations and experimental results informed that the elasticity and strength of an individual SiC nanowire was much higher than that of bulk SiC. Therefore SiC nanowires are promising materials for application in nanodevices, optoelectronics, microelectronics, and nanocomposites. Extensive studies on SiC nanonstructures began in the mid-1990s. To date, SiC nanowires have been fabricated by several methods, mainly based on vapor-liquid-solid (VLS) growth mechanism with assistance of metal catalysts (Fe, Ni, Al, etc.) and vapor-solid (VS) growth mechanism. For instance, SiC nanowires have been synthesized from carbon nanotubes as the template, by chemical vapor deposition, arc discharge, laser ablation, and sol–gel method.

Up to now, there is no report about the synthesis of SiC nanowires from the reaction between CH$_4$ gas and Si powder. In this study, the synthesis of $\beta$-SiC/SiO$_2$ core-shell nanowires through simple thermal evaporation of Si powder among flowing CH$_4$ gas is reported.

2. Experimental procedure

A silicon nanopowder (average particle size ~50 nm) of 99% nominal purity was used as a raw powder. The synthesis of SiC nanowires was carried out in a horizontal mullite tube furnace. A mullite boat containing Si nanopowder was placed in the middle of the tube furnace. After pumping the tube to a pressure below 1.33 Pa, Ar gas was fed at a flow rate of 0.6 l/min into the tube to maintain an inert atmosphere. Then the tube was heated to 1473 K, and H$_2$ (purity: 99.999%) at a flow rate of 20 sccm was fed for 2 min before flowing of CH$_4$ (purity: 99.99%) at a flow rate of about 400 sccm for 1 min. CH$_4$ gas was fed 1 min with 5 min interval until 1623 K. At 1623 K, CH$_4$ gas was fed only 30 s and alternated with closing of the flow meter for 10 min until the middle of the soaking. From the middle of the soaking at the maximum temperature until cool down, CH$_4$ and H$_2$ were not fed into the mullite tube. Ar gas was continuously fed until cooled down to room temperature.

After 1 h of growth, soft gray powder covered with black crust was formed in the boat. X-ray diffraction (XRD, Cu Ka, PW 1700, Philips, the Netherlands), scanning electron microscopy (FE-SEM, field-emission type, S–4800, Hitachi, Japan), transmission electron microscopy (TEM, H–9000, Hitachi, Japan), energy dispersive X-ray (EDX) spectroscopy on scanning TEM (STEM), and infrared-ray spectroscopy (FT-IR, Fourier transform type, FT/IR–460Plus, JASCO, Japan) were used to characterize the synthesized nanowires. Specimen preparation for TEM observation was as follows. The specimens were softly ground in a SiC mortar, and they were dispersed into ethanol. Ultrasonic was applied to disperse wires and then the suspension was dropped onto a lacy micro grid. The micro grid was left till dry at room temperature.

3. Results and discussion

After the reaction at 1623 K for 1 h, two layers of products were obtained in the mullite boat. The XRD patterns of the products are shown in Fig. 1. The XRD pattern of the soft gray powder (bottom layer) illustrated that there were only four main strong peaks at 2θ(Cu Kα) = 35.93°, 41.65°, 60.37° and 71.99°, which were in good agreement with reflections of the (111), (200), (220) and (311) planes of cubic $\beta$-SiC (Fig. 1(a)). A small forward peak of the highest intensity peak (111) seemed to be resulted from the stacking faults as mentioned in references. Black crust (top layer) exhibited peaks of $\beta$-SiC along with low crystallinity graphite (2θ(Cu Kα) = 26.19°, 44.05° and 53.87°)

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The top layer product contained un-reacted carbon. Therefore, we emphasized on the bottom layer product, which was characterized furthermore.

Figure 2 shows a typical FE-SEM image of the soft gray powder. It was clear that a large quantity of randomly distributed wire-shaped products (hereafter it was called as nanowire) was formed. Lengths of the nanowires were up to several tens of micrometers and diameters were 65–85 nm. A typical TEM image of nanowires is shown in Fig. 3. It can be observed that there were two kinds of wires. One of them was typical wires which did not have nanoparticles or caps at the tip of wires, and the other one was un-typical wires with caps at the tip of wires (pointed by white arrow). The nanowire with a cap scarcely existed. Figure 4(a) is a high magnification TEM image of a typical nanowire, clearly revealing that the nanowire consisted of a dark-contrasted inner core of 50–70 nm in diameter and a light-contrasted outer shell of ~15 nm in thickness, and the dark core was positioned at the center of nanowire. The selected-area electron diffraction (SAD) patterns of core and shell parts are shown in Figs. 4(b) and (c), respectively. The SAD pattern from the core part could be indexed with the $\beta$-SiC crystal with twins and the fiber axis direction was found to be $[111]$ of $\beta$-SiC. Only diffused spots ($d =$ 0.34 nm and 0.21 nm) sited along and perpendicular to the fiber direction, respectively, were detected from a shell layer, indicating incomplete crystallinity.

Figures 5(a) and (b) show the result of STEM-EDX from core and shell parts, respectively. The EDX spectrum obtained from the core of a nanowire confirmed that this part should be SiC since appearance of Si, C, O and Cu peaks. Cu peak was caused from a copper grid sample holder and column material of the equipment. Whereas the EDX spectrum collected only from the

![Fig. 1](image1.png)

![Fig. 2](image2.png)

![Fig. 3](image3.png)

![Fig. 4](image4.png)

![Fig. 5](image5.png)
shell layer exhibited that the shell layer was also composed from Si, C, O and Cu peaks, the intensity of O peak from the shell layer was much higher than that from the core of the wire.

A TEM image of an un-typical nanowire with cap attached at the tip is shown in Fig. 6. The shape of un-typical nanowires looked like a match. The composition of stalk and cap was measured by STEM-EDX. The EDX spectrum (not shown here) from a stalk and a cap of the wire indicated that both spectrums contained Si, C, Cu, and O peaks. Furthermore, Fe was only detected from a cap. However, the intensities of Si and C in stalk area were much higher than in the cap area. These results can be explained as that the stalk of a match wire was SiC which was grown by an aid of Fe at the cap.

In addition, FT-IR was used to confirm composition of the nanowires. FT-IR spectrum of the synthesized SiC nanowires is shown in Fig. 7. There were two absorption peaks at around 1100 and 469 cm\(^{-1}\), which were matched with Si–O stretching vibration, and the absorption peak at around 805 cm\(^{-1}\) corresponded to Si–C stretching vibration. The results were consistent with the previously reported value. An absorption peak at around 805 cm\(^{-1}\) corresponded to the transversal optic (TO) mode (Si–C stretching vibration) and shoulder at around 890–950 cm\(^{-1}\) (marked by small square) was related to the longitudinal optic (LO) vibration mode. Together with STEM-EDX, TEM and XRD analyses, we believe that the produced nanowires consisted mainly of SiC core wrapped with thin layer of low crystallinity SiO\(_2\).

Since difference in morphologies of two kinds of nanowires was obvious, growth mechanisms of these products should be different. The growth of the typical nanowires should not be synthesized from conventional metal catalized VLS growth mechanism, because there were no cap catalyst at the tip of nanowire, whereas the un-typical nanowires with a cap at the tip of nanowire should be grown by the VLS mechanism. A little amount of Fe impurity in the Si nanopowders (less than 15 ppm), the starting material, can act as a self-metal catalyst to create liquid droplets.

As mentioned above, the present SiC nanowire consisted of central SiC part and surrounding SiO\(_2\) part. The origin of oxygen in this system may be attributed to two sources. The main source should be attributed for surface SiO\(_2\) on the Si raw powder. Actually the oxygen content of the raw powder was measured to be 23 mass\%, due to its very small particle size. The other source of oxygen may be arisen from materials inside furnace at high temperature, such as the mullite (3Al\(_2\)O\(_3\) · 2SiO\(_2\)) boat and the mullite tube were used in the present study. To confirm the source of oxygen, a boron nitride boat instead of the mullite boat was used to assure oxygen occurrence from the mullite boat. FE-SEM image of as-synthesized products using the same Si nanopowder put in the boron nitride boat and then synthesized at 1623 K for 1 h is shown in Fig. 8. The amount of nanowires was much smaller than the experiment conducted under the same synthesis conditions except for the mullite boat (Figs. 2 and 3). It was clear that the effect of O\(_2\) from mullite boat promoted formation of SiC nanowires. It was supposed that the oxygen from the raw powder should also be effective.
At present, the formation reaction of SiC core and SiO$_2$ outer shell would be considered as follows. The SiO vapor and evaporated Si reacts with CH$_4$ gas to form SiC. Then, the as-grown SiC nanowires are oxidized to form the SiO$_2$ surface layer by residual O$_2$ in the system or H$_2$O, which is probably a by-product of the formation reaction of SiC. The effects of synthesis conditions on the nanowires formation and the details of the growth mechanism of typical nanowires are under consideration.

4. Conclusions

The simple thermal evaporation technique of Si in flowing CH$_4$ gas has been shown to be one method which is able to synthesize the SiC nanowires. The following conclusions were obtained based on the experimental results of the current work:

1. The reaction of Si nanopowders and CH$_4$ gas at 1623 K in a mullite tube furnace could produce a large quantity of randomly distributed β-SiC/SiO$_2$ core-shell nanowires.

2. The synthesized typical nanowires consisted of single crystalline β-SiC core of 50–70 nm in diameter and a uniform wrapped layer of low crystallinity SiO$_2$ of ~15 nm in thickness, and their lengths are up to several tens micrometers.

3. The fiber axis of the nanowire was [111] of β-SiC.

4. Oxygen from the experimental setup or the raw powder should be a key factor to synthesize the core/shell nanowires.

References