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A novel method for massive fabrication of β-SiC nanowires

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Abstract Silicon carbide nanowires (NWs), that were over 200 μm in length and 20–200 nm in diameter, were prepared by high-pressure reaction from SiBONC powder tablets. Annealing temperatures between 1,500 °C and 1,600 °C and Si/B molar ratios between 70:30 and 60:40 were suitable for the growth of the nanowires. The nanowires were fabricated by in situ chemical vapor growth process on the tablets. The SiC nanowires were identified as single crystal *β*-SiC. The analysis of X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed the single crystalline nature of nanowires with a growth direction of <111>. Massive growth of single crystalline SiC nanowires is important to meet the requirements of the fabrication of SiC nanowire-based nanodevices.

Introduction

One-dimensional SiC materials, i.e., nanowires and nanorods, are of great interests for many applications due to their excellent properties, such as high mechanical strength, high thermal stability, high thermal conductivity and large band gap [1, 2]. High strength and stiffness combined with a high aspect ratio of SiC nanowires make them very effective reinforcement for various composites. The strength of SiC nanowire has been found to approach the theoretical strength and is substantially larger than that found in bulk SiC [3]. Silicon carbide nanowires were first synthesized in 1995 by using carbon nanotube as a template [4]. Han et al. [3] developed a process for producing SiC nanowire via a reaction between carbon nanotubes and a Si–SiO_2 powder mixture. Carbothermal reduction of sol–gel derived silica aerogel containing carbon nanoparticles has also been used to grow SiC nanowires with diameters range from 30 nm to 70 nm [5]. Recently, Zhou et al. [6] grew *β*-SiC nanowires with diameters ranged from 10 nm to 30 nm on silicon substrates by employing hot-filament chemical vapor deposition (HFCVD).

The methods mentioned above are generally either of high cost or, to some extent, complicated. Meanwhile, the inability to control the chemistry in the synthesized SiC nanowires is also evident. These drawbacks may limit the massive fabrication and applications of SiC nanowires. Furthermore, from the viewpoint of nanomanipulation, substantial challenges might also be realized. In the situ fabrication of SiC nanowires, in some designed substrates such as powders contained SiC phase might provide a solution to the nanomanipulation problem. Such an effort has been made in recent work by Salama et al. [7], in which a laser direct-write process to fabricate carbon rich SiC nanoribbons in a 4H-SiC single crystal wafer was discussed. The proposed laser process enables the fabrication of nanoribbon-SiC heterostructures directly within the SiC wafer, and thus eliminated the need for nanostructure transferring from one medium to another, although a graphite layer was also produced.

In this paper, we describe a research of *β*-SiC nanowires, generated by high-pressure reaction via using SiBONC ceramic powder tablets. A sample of situ chemical vapor growth method for fabricating *β*-SiC nanowires

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on SiBONC ceramic powder tablets was reported. This process demonstrates many merits. For example, it is easy to control the composition, dimensions and the morphology of the resulting nanowires, secondly there is no need of a catalyst for nanowires growth, and finally there is high feasibility for a massive production of the nanowires.

Experimental procedure

Polymer synthesis

SiBONC polymeric precursor $[B_3(NPh_x)_xSi_3O]_n$ was prepared based on the overall reaction:

$$[SiOCl_x]_n + PhNH_2 + BCl_3 \rightarrow [B_3(NPh_x)_xSi_3O]_n + HCl \tag{1}$$

The Si/B molar ratios selected were 85:15, 80:20, 70:30 and 60:40.

Chloro-polysiloxane $[(SiOCl_2))_n]$ was prepared in a translucent airtight container in lab at room temperature, through the reaction between $SiCl_4$ and PhCHO with a volume ratio of 1:1. The silicon chloride ($SiCl_4$), phenyl aldehyde (PhCHO), toluene ($PhCH_3$), boron trichloride (BCl_3) and phenylamine ($PhNH_2$) are commercial analytically pure chemical reagents. All chemical reagents were purified by distillation before experiments. In the synthesis of the precursor, $[(SiOCl_x)_n]$ was first dissolved in toluene ($C_6H_5CH_3$) at a temperature near 80 °C. A specific amount of phenylamine was then added into the solution drop by drop. Then solution became turbid, and HCl released, which indicated that reaction had occurred between the phenylamine and the $[(SiOCl_x)_n]$. After completion of the first reaction, the BCl_3 gas was slowly introduced into the above polymer solution to promote reaction, where we also detected hydrochloride (HCl) in the tail-gas absorber. Finally, the residual solvent was removed by condensation at a temperature near 120 °C, and the end polymer precursor was synthesized. The precursor was a brown, hard glassy solid. Samples of polymer precursors turned more yellow and solidified on prolonged exposure in air.

Pyrolysis polymer precursor

Samples of polymer were pyrolyzed in flow N_2 to 1,000 °C in silica tube furnace. Samples were typically heated at rate of 3 °C/min.

Preparation of the SiC nanowires

In the previous work, a thick layer of SiC nanowires was found covering over the gas pressure sintered SiBONC ceramic powders. However, SiC NWs were mixed with matrix powders, separating them is very hard. Therefore, we designed a steel mold; the powders were molded into small tablets with cold press. When heat treatment was over, matrix was sintered and has some strength, the SiC NWs were easily removed from matrix and product ratio was increased to previous method.

The tablets with different chemical compositions were only put into a graphite crucible and were calcined in gas pressure furnace to 1,500–1,600 °C in argon (Ar) atmosphere, with gas pressure of 19.7384 atm at final temperature (heating rate $T < 1{,}400$ °C: 10 °C/min, $T > 1{,}400$ °C: 2 °C/min, dwell time 1 h). The nanowires can be grown on tablet surfaces with the Si/B ratio of 60:40 and 70:30 ceramic powders. The schematic drawing of the furnace is shown in Fig. 1.

Figure 2 is the macroscopical photograph of the nanowires growth in the graphite crucible. It is found that the sintered bodies are covered with a thick layer of white aerogel-like matters, the NWs is removed by brush and collected for characterization.

Instrumentation

The X-ray diffraction (XRD) of the SiC nanowires was performed using a Philips instrument operating with Cu-Kα radiation ($\lambda = 1.54178$ Å) at 40 kV/50 mA. Transmission electron microscopy (TEM) and selected area electronic diffraction (SAD) were carried out on a Philips TECNAI 20 microscope operating at 200 kV. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were performed using Philips FEI Sirion microscope operating at 20 kV. Further structural and compositional analysis of individual NWs was performed using high-resolution transmission electron microscopy (HRTEM, JEM 3010).

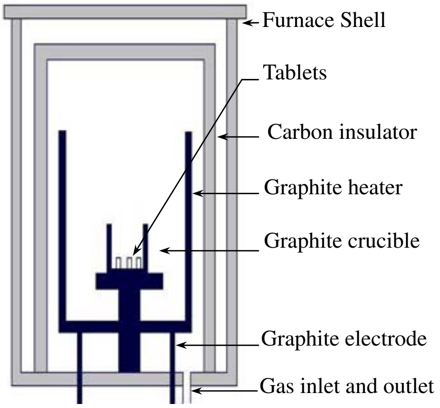

Fig. 1 Schematic drawing of the gas pressure furnace

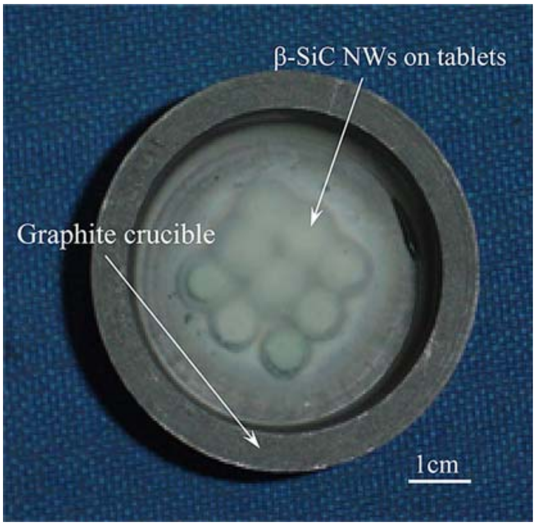

Fig. 2 Macroscopically photograph of the nanowires in graphite crucible after annealing

Results and discussions

Figure 3 shows the XRD patterns of the annealed specimen. From Fig. 3, three SiC peaks at 36°, 60° and 72° were observed, respectively, which can be attributed to the diffraction of SiC {111}, {220} and {311} planes, and indicate the formation of *β*-SiC. The peak at 26° arises from graphite layer {002}, and the graphite phase comes from the graphite crucible. This suggests that the crystallized SiC is fine crystallized. Therefore the produced nanowires mainly consisted of SiC.

To get the microstructure of these nanowires, SEM and TEM were employed. SEM morphologies and EDX patterns of *β*-SiC nanowires are shown in Fig. 4. It can be seen that most of the product exhibits wire-like structure and nanowires with diameter from 20 nm to 200 nm, length up to several millimeters. For technical convenience, thicker wires with diameter from 100 nm to 200 nm were selected for observation. EDX pattern of SiC nanowires is shown in Fig. 4b, confirming that it is only composed of two elements silicon and carbon.

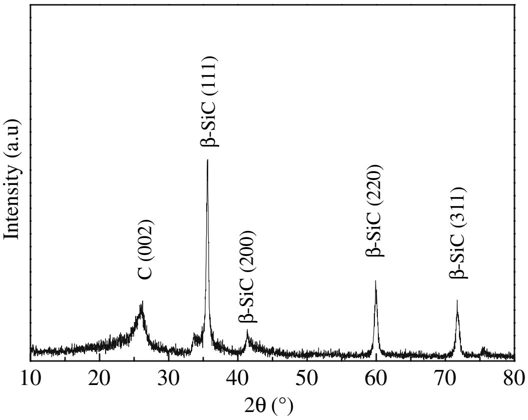

Fig. 3 XRD pattern of the nanowires

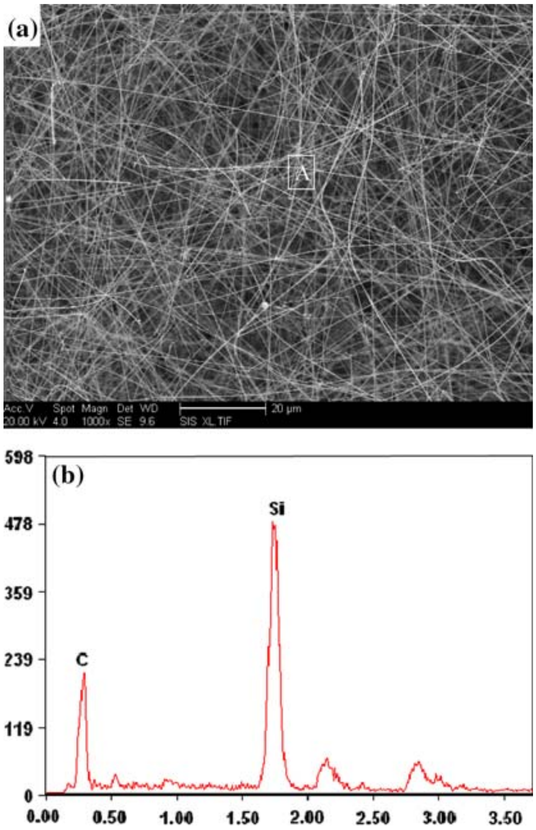

Fig. 4 SEM morphology and EDX pattern of the *β*-SiC nanowires (**a**) Overall morphology of the *β*-SiC nanowires, (**b**) EDX pattern of the area A

Figure 5a–c shows the TEM images and corresponding SAD patterns of the SiC nanowires. For TEM observation, samples were dispersed in alcohol solution, by an ultrasonic generator. The solution containing nanowires was dropped on copper grid coated with amorphous carbon, naturally dried? TEM image and SAD analysis indicate that nanowires consists of a single crystal *β*-SiC structure with growth along the <111> direction. Figure 5b inset shows clear microtwins in nanowires are found in the image. Similar stacking faults were often found by the TEM examinations in some other SiC nanowires [8]. The *β*-SiC crystal structure of nanowires was also confirmed by XRD analysis, as shown in Fig. 3.

Figure 6 shows the HRTEM image (a) and (b), and corresponding SAD pattern of SiC nanowires was shown in Fig. 6c. The HRTEM image and SAD patterns, recorded along the [011] zone axis, further confirm that the NW is single crystalline cubic zinc blend structures with a <111> growth direction.

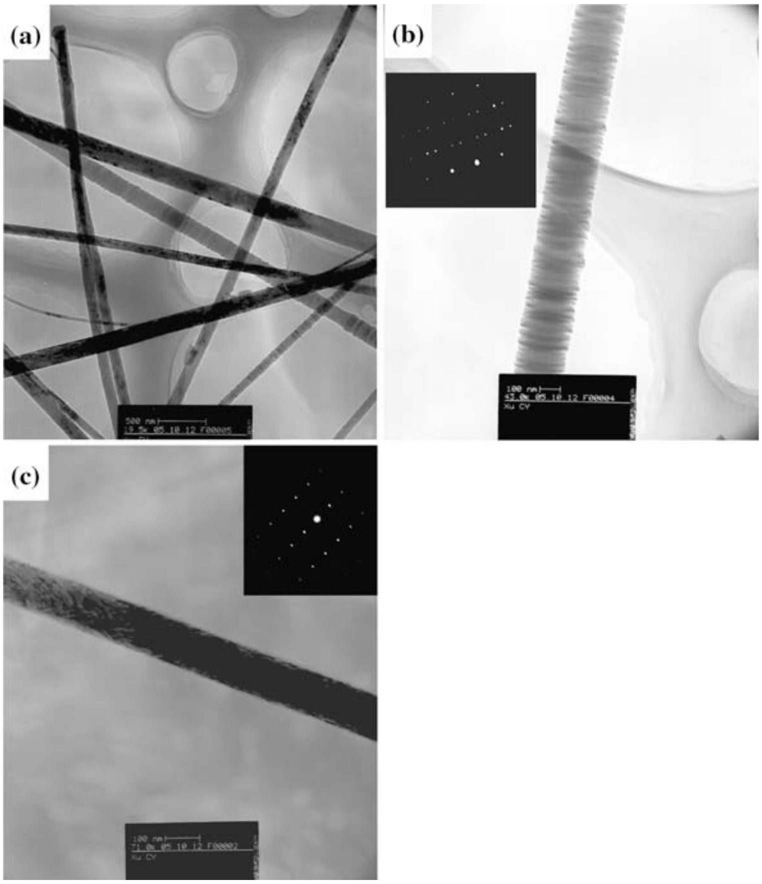

Fig. 5 TEM morphologies and SAD patterns of the β-SiC nanowires (**a**) Overall morphology of the nanowires, (**b**) The micro-twins in nanowires, (**c**) Normal surface of nanowires

TEM and XRD reveal that these NWs are also SiC with cubic zinc blend structure with a <111> growth direction. The self-aligned growth of NWs has been reported for ZnO [9] and GaN [10]. The alignment of these NWs is due to the epitaxial relationship between the substrate and the NWs. It has been proposed that the relaxation of stress at the interface between the substrate and the NW is responsible for the growth of self-assembled GaN NWs by enhancing the growth rate in the preferred growth orientation in the early phase of the three dimensional growth modes [11]. Since the generation of stress between Si/SiC or graphite/SiC interfaces would be expected, such a stress relaxation could contribute to the self-alignment of SiC NWs shown in this study.

The VLS mechanism is a well-accepted mechanism for growth of nanowires. However, SEM and TEM examinations suggest that nanowires in the present process are not grown by VLS mechanism, and liquid droplets are not found on the tips of the present nanowires, which is inherent with VLS mechanism.

The formation mechanism of β-SiC nanowires in present method is proposed as follows. As gas pressure furnace was heated to 1,500 °C, the silicon carbon thermal reaction would take place, according to the Eqs. 5–9. The calculation of free energy change in silicon and graphite reaction was calculated by Gibbs–Helmholtz equation (2–4),

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

$$\Delta G_T^o = \sum \Delta H_0 - T\sum \Delta S_0 + \sum \int_{298}^{T} \Delta C_P \mathrm{d}T - \sum \int \Delta C_P T^{-1} \mathrm{d}T \tag{3}$$

$$\Delta H = \Delta H_0 + \int_{T_0}^{T_m} C_{p1} \mathrm{d}T + f\Delta H_m + \int_{T_m}^{T} C_{P2} \mathrm{d}T \tag{4}$$

From the calculation, reaction temperature can be obtained about 1,493 K; however, in gas pressure furnace Ar pressure is 19.7384 atm, which can restrict the formation of CO. Therefore, reaction temperature can be raised.

$$\mathrm{C\ (s) + SiO_2(s) \rightarrow SiO\ (g) + CO} \tag{5}$$

$$\mathrm{SiBONC(s) \rightarrow Si_{1-x}BO_{1-y}NC_{1-z}(s) + aSiO(g) + bCO(g)} \tag{6}$$

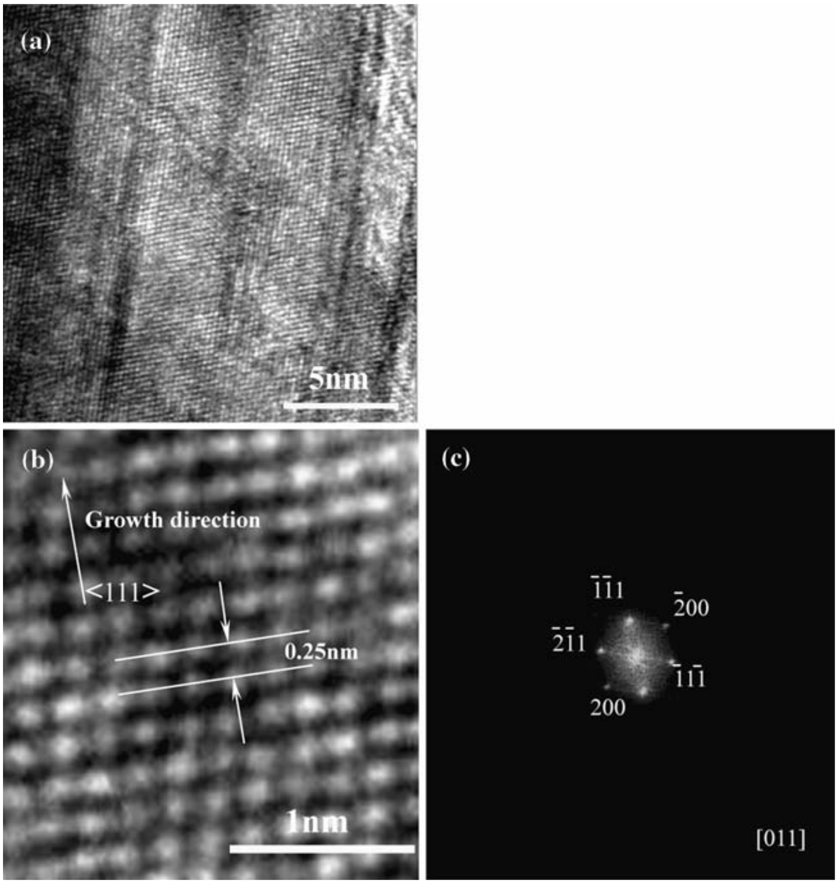

Fig. 6 HRTEM morphologies and SAD pattern of *β*-SiC nanowires (**a**) HRTEM image, (**b**) Lattice image, (**c**) Corresponding SAD pattern

$$SiO(g) + CO(g) \rightarrow SiC(nuclei) + O_2(g) \tag{7}$$

$$2SiO\ (g) + 6CO(g) \rightarrow 2SiC(nanowires) + 4CO_2\ (g) \tag{8}$$

$$CO_2\ (g) + C(s) \rightarrow 2CO(g) \tag{9}$$

Equation 5 represents a solid–solid reaction. Since heater and container of powder tablets are graphite, carbon atom can be sublimed in furnace. In addition, in reaction process, the underside of graphite cylinder was very close to the SiBONC nanopowder. Therefore, the partial pressure of gaseous SiO produced in the graphite cylinder will be very high. When gaseous SiO meets with activated carbon atoms on tablets, SiC nanoparticles may be formed by reaction Eq. 6.

These SiC nanoparticles may serve as the SiC nuclei for further growth of straight SiC nanowires. In the process of SiC nanowires growth, Si and C may be further provided via Eq. 6. The CO_2 vapor generated can further partake in reactions, which was shown in Eq. 8.

From reactions (5–9), it is observed that the product of CO vapor is of a positive feedback characteristic. A condition of supersaturation of CO vapor will be formed. According to the kinetic growth mechanism proposed in Ref. [12], with the help of a supersaturation of CO vapor, SiC nanowire may grow along a fixed axis.

According to the analysis above and experimental observations, the growth process of present SiC nanowires might be illustrated as randomly distributed nanoparticles on the SiBONC tablets first formed at the initial deposition from reaction (6), followed by preferred deposition of SiC along the <111> direction. After a period of time, the growth of the SiC nanowires might be stopped due to a fluctuation in the local supersaturation. The diameter of the nanowires is likely to be determined by the size of initial nanoparticles. The surface energies of {111} planes in *β*-SiC is about 0.28 erg/m^2 (around 1,373 K) which is much lower than those of other planes such as the {110} (0.35 erg/m^2) and {211} (0.40 erg/m^2) [13]. Therefore, the SiC nanowires grew preferentially along the <111> direction to maintain the lowest growing energy. SiC nanowires/whiskers growing along the <111> direction have been reported in several studies [2, 5, 14–16].

Layer growth is a general phenomenon associated with supersaturation [17]. Under this condition, SiC can also grow along the directions other than the original <111>

direction. This might explain the layer growth behaviors of the SiC nanowires in Fig. 5b. The fault (microtwins) growth might have resulted from a fluctuation of the kinetic growth condition due to fluctuation of supersaturation, which would disturb the balance between growths along different directions. It is also possible that when local supersaturation becomes appropriate, an existing nanowire would begin to grow again but in a direction different from the original one. Continuous growth of SiC nanowires along <111> direction might be explained as a succession of depositions of Si and C atoms on {111} ''seeding'' surface in a layer-by-layer process. The growth front plane alternates between layers of the same kinds of atoms, say, first Si then C, and so on. A fluctuation of the kinetic condition might cause a change in stacking sequences, and thus stacking faults result in the nanowires. The stacking faults (microtwins) have a lower energy than that of the β-SiC [18]; therefore, they are helpful in maintaining a lower growth energy of the nanowires.

Therefore, we suggest that the growth of SiC in this work is an epitaxial growth of β-SiC nanowires on some random spots of the surface of SiBONC powder tablets. Other related products, such as carbon powders, amorphous carbons and chains connected by SiC nanowire are not found among the final products. This shows that the present method is superior to HFCVD, carbothermal reduction method and floating catalyst method. Carbothermal reduction method, using amorphous carbon as carbon resource, needs a long reaction time [19–22]. HFCVD [23] and the floating catalyst method need ferrocene [20–24] and iron particles [25–27] as catalyst, respectively.

Conclusions

A novel method for growth of SiC nanowires on SiBONC powder tablets has been developed. β-SiC nanowires with diameters of 20–200 nm and large aspect ratio have been successfully synthesized by annealing SiBONC ceramic powder tablets under gas pressure atmosphere. A composition of Si/B with ratio between 70:30 and 60:40 and temperature with a range of 1,500 °C and 1,600 °C are suitable for growth of these nanowires. The SiC nanowires were identified as single crystal β-SiC with growth along the <111> direction. No oxygen or other chemical impurities were detected in the nanowires. In situ applications of β-SiC nanowires in ceramic matrix composites, such as SiBONC composites are proposed. The formation of SiC nanowires maybe due to a vapor–solid (VS) mechanism, where SiC nano-sized particles are precipitated from an amorphous SiBONC matrix acting as nuclei for nanowires, and thermal decomposition of SiBONC provides the main resource (SiO and CO) for SiC nanowires growth.

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