Gas pressure atmosphere annealing: A novel method for the preparation of SiC nanowires

X Zhang1,3,4*, B Zhong2, L Liu1, X Huang1, G Wen1,2, Y Huang3, and J Bollmann1,4

1 School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, China
2 School of Materials Science and Engineering, Harbin Institute of Technology, Weihai, China
3 School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, China
4 Institute of Electronic and Sensor Materials, TU Bergakademie Freiberg, Freiberg, Germany

E-mail: zhangxiaodong@hit.edu.cn

Abstract. Silicon carbide nanowires were fabricated by gas pressure annealing of SiOC nanocomposite powders, which were synthesized by pyrolysis of a SiO2 - sucrose gel. The reaction was carried out in an atmosphere sintering furnace without any additives. The nanowires have pronounced homogenous diameters smaller than 100 nm and lengths of up to several millimetres. The X-ray diffraction pattern indicates the formation of the β-SiC phase and transmission electron microscopy analysis show the monocrystalline structure of the nanowires.

1. Introduction

In the last years one-dimensional quantum wires found considerable interest in low-dimensional physics and materials research due to their promising applications in nanoelectronics, micromechanics, field emission, and nanocomposites [1–3]. Among one-dimensional quantum wires, silicon carbide (SiC) nanowires attracted increasing interest during the past decade [4]. Recently, elaborated measurements, combining atomic force microscopy and lithography techniques, indicates that the strength value of SiC nanowires is about two times higher compared to the value of SiC whiskers with micrometre diameter [5, 6]. Furthermore, SiC is an important wide band-gap semiconductor with outstanding properties, such as high disruptive strength, high thermal conductivity, high saturation drift velocity, and excellent physical and chemical stability [7]. The combination of these distinctive physical and chemical properties make SiC nanowires a promising candidate for the fabrication of various nanoscaled devices [8–10].

However, most syntheses of SiC nanowires are quite complicated, difficult to control, and catalytic metal additives are usually essential. Therefore, the application of SiC nanowires is noticeable

* To whom any correspondence should be addressed
restricted so far. In this paper, a novel method for the synthesis of SiC nanowires is proposed and the preparation and structural characterization of such SiC nanowires are presented.

2. Experimental

2.1 Synthesis of SiOC nanocomposite
Sucrose and silica sol where used as starting materials to synthesize SiOC nanocomposite in the following way: At first, sucrose was intermixed with silica sol by magnetic stirring. Next, the resulting sol was converted into dry gel at 90°C. Finally, a SiO\textsubscript{3}C nano-composite is obtained by pyrolysis of the dry gel at 900°C for 30 min in a quartz tube under flowing nitrogen. The final powders are black in colour, amorphous in structure and nano-scaled in particle size.

2.2 Growth of SiC nanowires
The SiOC nanocomposite was annealed in a graphite crucible for 60 min under argon cover atmosphere in a gas pressured furnace at 1500°C. The initial argon pressure was 0.5 MPa. The nanowires grew at the surfaces of the powder and could be easily collected by brushing them from the sintered body.

3. Results and Discussion
A high-resolution scanning electron microscopy (SEM) image, shown in Figure 1, reveals that the SiOC nanoparticles are quite homogeneous in size. The diameter varies from 20 to 50nm. As a result, the SiOC powders have a very large specific surface and will exhibit a high reaction activity. Figure 2 shows the XRD pattern of SiOC powders, indicating that the powders are amorphous. Analysis of element yields that the molar ratio of Si:O:C is 1.101:2.032:2.907 whereas the percentage of impurities is less than 0.7wt%.

![Figure 1. SEM of SiOC nano-powders](image1.jpg)

![Figure 2. XRD pattern of SiOC nano-powders](image2.png)

The SEM morphologies and EDX patterns of the β-SiC nanowires are shown in Figure 3. Obviously, most of the products are wire-like shaped with diameters ranging from 80 to 120 nm and lengths up to several millimetres. The EDX patterns (see insert of Fig.3a) of the SiC nanowires confirm that the wires consist of Si, C and a small amount of O as well.

XRD measurements of bulk nanowires (on the sintered composite substrate) are presented in Figure 4 to identify the overall structure. The diffraction peaks can be indexed to a cubic structure with a lattice constant of 0.4358nm, in well agreement with reference values for β-SiC (JCPDS Card. No. 29–1129). The observed peaks at 35.8°, 60.1° and 71.8° are diffractions from (111)-, (220)- and 311)-lattice planes of SiC crystal, respectively.
Figure 3. SEM morphologies of the β-SiC nanowires

The high intensities of the diffraction peaks relative to the background signal indicate the high purity cubic β-SiC phase of the wires. However, the peak at 21.6° is the diffraction of the (101) planes of SiO₂ (JCPDS Card. No. 83–1403), which probably originates from a fractional crystallization of the SiOC powder.

Figure 4. (a) XRD pattern of the SiC nanowires with substrate

Figure 5. (a) TEM morphology of the SiC nanowire and (b) the corresponding SAED

To characterize the structure of the wires in more detail, transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were taken. Figure 3a shows a typical TEM image of the SiC nanowires, revealing that the nanowire is very uniform in diameter. The surface of the SiC nanowire is very clean, without any coating of amorphous materials and is very smooth. The corresponding selected-area electron diffraction pattern (Fig.3b) verifies that the nanowire is in a single crystalline phase. This spot pattern is due to the cubic β-SiC structure and indicates that the nanowires are perfectly crystallized.

Thermal analysis (TG) of the SiOC nano-powder was performed under argon ambient to gain more insight into the growth mechanism of SiC nanowires. DSC-TG curves (see Fig.6) show a significant weight loss above 1315°C and (endothermic) minima at 1245°C, 1315°C, 1412°C, and 1426°C, which are typically for the occurring reactions. We found initial reaction temperatures much lower than reported data in ref. [14] (see Tab.1).
From our experimental results the mechanism for the SiC nanowire growth will be the following one. The formation of SiC is an epitaxial growth starting on some random distributed spots at the surfaces of the SiOC powder matrix. During the carbo-thermal reduction, reaction (1) may start at 1493K [14], which introduces the nucleation of SiC. With increasing temperature, silicon monoxide (SiO) gas and carbon monoxide (CO) gas is generated by reaction (2) to (4). The SiO(g) and CO(g) now reacts directly at some nucleation sites (presumably β-SiC crystallites at the surface of the powder) to produce β-SiC nanowires via the vapor reaction (5). Due to thermodynamic principle, the nanowires grew along the [111] direction of β-SiC which is the preferential growth direction to minimize Gibbs free energy.

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\begin{align*}
\text{SiO}_2(s) + 3C(s) &= \text{SiC(s)} + 2\text{CO(g)} \quad (1) \\
\text{SiO}_2(s) + 2C(s) &= \text{Si(l)} + 2\text{CO(g)} \quad (2) \\
\text{SiO}_2(s) + 2C(s) &= \text{SiO(g)} + \text{CO(g)} \quad (3) \\
\text{CO}_2(g) + C(s) &= \text{CO(g)} \quad (4) \\
\text{SiO(g)} + \text{CO(g)} &= \text{SiC(s)} + \text{CO}_2(g), \quad (5)
\end{align*}
\]

where (s), (l) and (g) refer to the solid, the liquid and the gaseous state, respectively.

Equation (1) is either a purely solid-solid or a liquid-solid reaction (above 1450°C, quartz melts).

In our study, both SiO2 and carbon exist in nano-sized and amorphous state so that the melting point of SiO2 and the initial reaction temperature might be lowered by about 200°C [14-16]. Moreover, the high argon gas pressure used here ensures the saturation of SiO gas and CO gas.

| Reaction equation | \( \Delta G \) (J/mol) | Reaction temperature (K) |
|-------------------|----------------|--------------------------|
| \( \text{SiO}_2+2C = \text{Si}+2\text{CO} \) | 151865-8T | 1814 |
| \( \text{SiO}_2+3C = \text{SiC}+2\text{CO} \) | 116300-76.95T | 1493 |
| \( \text{SiO}_2+\text{SiC} = 3\text{Si}+2\text{CO} \) | 258870-106.63T | 2240 |
| \( \text{SiO}_2(l)+C = \text{SiO}+\text{CO} \) | 144050-69.36T | 2070 |
| \( \text{SiO}_2(l)+\text{Si(l)} = 2\text{SiO(g)} \) | 133420-53.25T | 2505 |
| \( \text{SiO}_2(l)+\text{Si(g)} = 2\text{SiO(g)} \) | 58950-35.66T | 1653 |
3. Conclusions
In summary, large quantities of high-purity crystalline β-SiC nanowires could be synthesized in an atmosphere sintering furnace without any catalytic additives. The results show that the nanowires with diameter below 100 nm are oriented along the [111] direction and are in the single-crystalline β-SiC phase without any wrapping of amorphous material. The demonstrated manufacturing process has inherent advantages, including a simple production procedure, low-cost raw materials, lower synthesis temperature and a high yield, and can be easily scaled-up.

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