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Preparation and dielectric properties of SiC nanowires self-sacrificially templated by carbonated bacterial cellulose

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ABSTRACT

SiC nanowires were synthesized by the infiltration process of reactive vapor Si in Ar atmosphere at 1350–1450 °C, using carbonated bacterial cellulose (CBC) as carbon template and a reactant. Scanning electron microscopy (SEM), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and vector network analyzer were employed to characterize the samples. The diameter of the resulting β-SiC nanowires changes with calcination temperatures, specifically, 35–60 nm for 1350 °C, 40–80 nm for 1400 °C, and 30–60 nm for 1450 °C. The β-SiC nanowires obtained at 1400 °C possess the highest ε″ of complex permittivity.

1. Introduction

In recent years, more and more researchers have been considerably interested in SiC nanowires due to its excellent properties for chemical resistance, wide band gap, high electron mobility, high thermal stability and high saturated carrier drift velocity [1–4]. At the same time, SiC nanowires have important applications in the electromagnetic interference shielding. It can meet the technical requirements for various form materials, such as thin layer, light weight, strong, and wide frequency range [5].

Many synthesis methods and dielectric properties of SiC nanowires have been reported. Wong et al. [6] obtained SiC nanowires by using hot-filament-assisted chemical-vapor deposition with a solid silicon and carbon source. Liang et al. produced bulk quantities of β-SiC nanowires from the mixture of activated carbon and sol–gel derived silica embedded with Fe nanoparticles [7]. Jänis et al. synthesized SiC nanowires with Si, C, and O by the "shape memory process" technique [8]. The nanowires prove that the real component ε′ and imaginary component ε″ of the complex permittivity depend on the C content. However, to date, few synthetic approaches for SiC nanowires by the sacrificial template method have been reported, although the method has been widely used for the synthesis of various tailored SiC nanostructures including nanotubes [9], macroporous [10] and mesoporous [11,12] structures.

Our previous work with bacterial cellulose (BC) reported that the carbonated bacterial cellulose (CBC) obtained from BC possesses a three-dimensional network structure (see Fig. 1). In this paper, we reported the synthesis of SiC nanowires by using CBC as a template. The synthesis occurs by the infiltration process of reactive vapor Si at 1350–1450 °C in Ar atmosphere without use of any catalyst in the presence of CBC. The phase, morphologies and detail structure of the samples were investigated. The electric permittivity of the samples in the frequency range of 0.1–14 GHz was also discussed.

2. Experimental

2.1. Sample preparation

CBC was obtained by sintering dried BC at 1000 °C. CBC was mixed with commercial silicon powder (99.0%, crystalline, less than 300 mesh, Tianjin Fuchen Chemical Reagents Factory) in alcoholic solution, and then stirred for 3 h. The molar ratio of CBC and Si in the mixture starting material is 4:1. After being dried at 80 °C, the mixture was loaded into an alumina boat, and subsequently placed at the center of an alumina tube furnace. The dried mixture was heated up to 1350–1450 °C and then held for 4 h to synthesize SiC nanowires. Reaction occurred in argon atmosphere and the flow rate was maintained at 150 ml min^{-1}.

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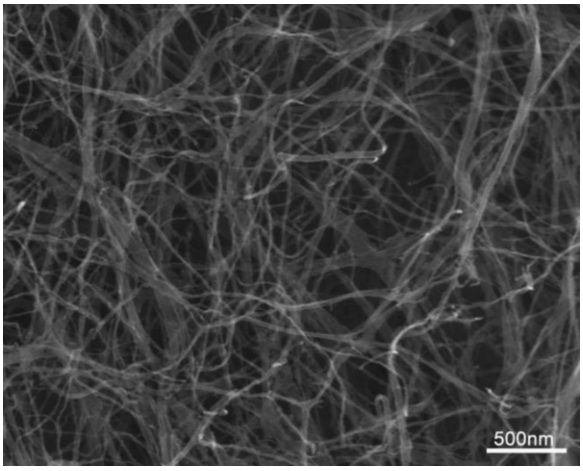

Fig. 1. SEM image of CBC obtained by sintering dried BC at 1000 °C.

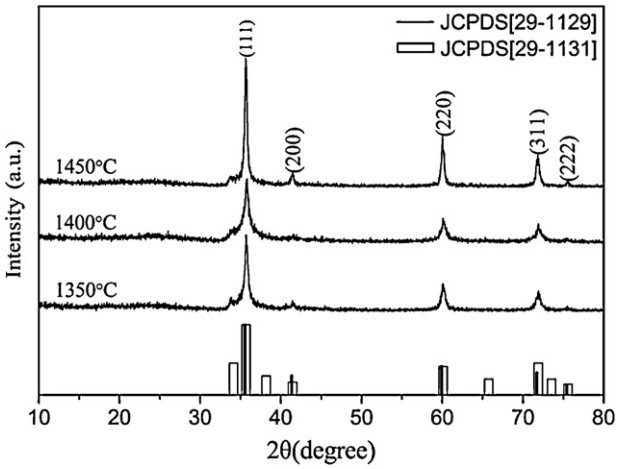

Fig. 2. XRD patterns of purified SiC synthesized at different calcination temperatures and reference data of β-SiC (black) and α-SiC (white) for comparison, taken from JCPDS ([29-1129] and [29-1131]). The samples were treated for 4 h for all temperatures.

Finally, the samples were heated at 800 °C in air for 4 h to remove excess carbon.

2.2. Measurements

Phase analysis of the samples was studied from 10° to 80° using an X-ray diffraction analyzer (XRD, Cu K-α, λ = 0.1514 nm, Rigaku D/max-RB, Japan). The surface morphologies of SiC nanowires were examined using a scanning electron microscope (SEM, LEO S440, Leica Cambridge Ltd, UK). The more detail structure of SiC nanowires was characterized using a transmission electron microscope combined with energy dispersive X-ray (EDX) and a high-resolution transmission electron microscopy (HRTEM) (TEM/HRTEM, Tecnai F20, FEI).

The dielectric parameters of the samples were measured by a vector network analyzer (E5071c, Agilent, USA) in a frequency range of 0.1–14 GHz. The powders were mixed with molten paraffin (80 °C) [13–15] and then pressed into special shapes with a 7.0 mm outer diameter and a 3.0 mm inner diameter. The mass ratio of SiC powders to paraffin was 2:1.

3. Results and discussion

The X-ray diffraction patterns of samples are shown in Fig. 2. Three strong peaks locate at $2\theta = 35.6°$(1 1 1), 60°(2 2 0) and 71.8°(3 1 1), separately. Compared with reference data, it is clearly that the observed peaks are in full agreement with those of the β-SiC (PDF No. 29-1129). A small shoulder at $2\theta = 34°$ with low intensity is attributed to a consequence of stacking faults of the β-phase [16,17]. At the calcination temperature up to 1450 °C, the diffraction peaks at $2\theta = 41.38°$ (2 0 0) and 75.49° (2 2 2) display apparently. This result indicates that β-SiC grows with an increase in temperature. In addition, no amorphous scattering curves and diffraction peaks of trace silicon are detected. It suggests that amorphous CBC and silicon are absent. Hence, the conversion of the mixtures into the β-SiC is rather complete.

Fig. 3 shows the scanning electron microscopy (SEM) images of the β-SiC nanowires obtained at different temperatures. It can be seen that the morphology of β-SiC replicates the nanowire configuration of the CBC (Fig. 1). The surface of β-SiC nanowires is very rough. The length of all β-SiC nanowires is about several micrometers and the average length obtained at 1400 °C is more than twice that at other two temperatures. The average diameter of β-SiC nanowires also changes with calcination temperatures, specifically, about 35–60 nm for 1350 °C (Fig. 3a), 40–80 nm for 1400 °C (Fig. 3b), and 30–60 nm for 1450 °C (Fig. 3c). This means that the preparation temperature of 1400 °C is suitable for large-size growth of β-SiC nanowires, 1350 °C may be too low to make the reaction generate entirely, and 1450 °C is possibly so high that SiC nanowires are melted. Meanwhile, it indicates that the length and diameter of β-SiC nanowire can be conveniently controlled with the reaction temperature.

To investigate more details of the structure of β-SiC nanowires, transmission electron microscope (TEM) combined with energy dispersive X-ray (EDX) analyses was performed. Fig. 4a shows a typical TEM micrograph of β-SiC nanowires prepared at 1450 °C for 4 h. The diameter of nanowires is in the range of 30–60 nm, consistent with the result of SEM image (Fig. 3c). The inset image in Fig. 4a shows the high-resolution TEM (HRTEM) image obtained from the same sample of Fig. 4a. The distance of the lattice is 2.52 Å, which can be attributed to the (1 1 1) atomic planes of

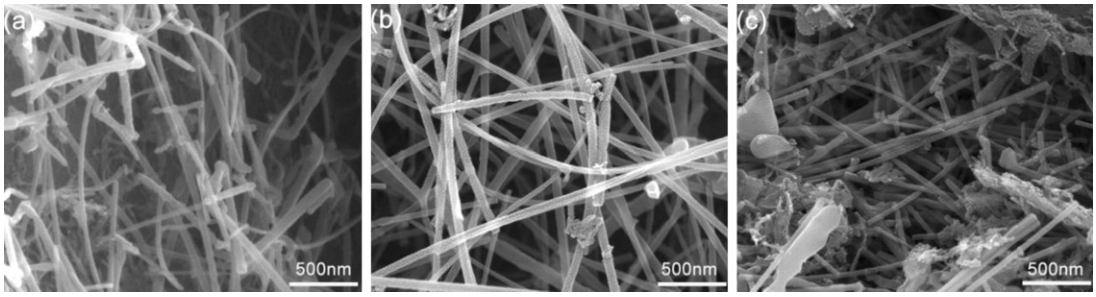

Fig. 3. SEM images of SiC nanowires prepared at different calcination temperatures (a) 1350 °C, (b) 1400 °C, (c) 1450 °C.