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Synthesis of blue-green photoluminescent β-SiC nanowires via a simple catalyst-free CVD technique

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ABSTRACT

β-SiC nanowires (NWs) have been successfully synthesized in the absence of Ar gas protection by a simple, catalyst-free chemical vapour deposition (CVD) using silicon, trace nanoscale SiO_2 particles, and phenolic resin powders as starting materials. The β-SiC NWs formed by a vapour-solid growth mechanism, with growth along the [1 1 1] direction. They were well-crystallized, with various morphologies (chain-bead, bamboo-shaped, and linear), and had lengths of up to dozens of microns and diameters of 80–650 nm. Moreover, they exhibited excellent blue-green photoluminescence properties due to the presence of stacking faults and amorphous SiO_2. This novel CVD technique is green, low cost, and suitable for large scale production of SiC NWs.

1. Introduction

SiC nanowires (NWs) have attracted much interest owing to their excellent mechanical, thermal, electrical, and optical properties [1–3]. They have prosperous applications in the fields of high temperature ceramics, microwave absorbers, optoelectronic devices [4], etc. In recent years, the synthesis of SiC NWs with different morphologies and their respective photoluminescence properties have drawn increasing interest. Previous researches have noted that SiC NWs with diameter-fluctuating (chain-bead, bamboo-shaped) and SiC/SiO_2 core-shell structures have excellent photoluminescence properties due to a high-density of stacking faults and an amorphous SiO_2 layer [5].

Diverse methods have been used to synthesize multi-morphology β-SiC NWs, including chemical vapour deposition (CVD) [6], carbothermic reduction [7], thermal evaporation [8], microwaves [9], arc discharge [10], etc. The simplest of these is CVD, especially using Si, SiO_2, or a Si-SiO_2 mixture as the main starting material. In the conventional CVD process, higher temperatures, catalysts, or molten salt, as well as Ar protective gas are generally required because more SiO_2 powder is used with a larger particle size [6]. However, the complicated process and expensive equipment are not suitable for large-scale production of SiC NWs in low cost. Moreover, the metal catalysts and molten salts used in these preparations are difficult to remove from the resultant SiC NWs, which may adversely affect the properties of the target products. Therefore, a greener, simpler, and more economical approach needs to be developed to synthesis SiC NWs with desirable photoluminescence properties.

In the present work, β-SiC NWs are synthesized by a simple catalyst-free CVD method at 1400 °C in the absence of flowing Ar gas, using phenolic resin powder, silicon powders, and trace nanoscale SiO_2 (nano-SiO_2) particles as starting materials. The morphology, crystal structure, and photoluminescence performance of the obtained β-SiC NWs are investigated. The novel CVD method is green, low cost, and suitable for large scale production, and there are few reports on this aspect.

2. Experimental

2.1. Materials

Si powder (purity 99 wt%, ≤40 μm, Anyang Oriental Metallurgy Co., Ltd.) and nano-SiO_2 particles (purity 99.5 wt%, average particle size ~50 nm, Evonik Specialty Chemicals Co., Ltd.) were used as silicon sources. Phenolic resin powder (residual carbon 57.5 wt%, ≤74 μm, Xinxiang Boma Co., Ltd.) was used as a carbon source. The weight ratio of Si to C was 1:3, and a trace amount (0.5 wt%) of nano-SiO_2 powder was added.

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2.2. Sample preparation

The nano-SiO_2 powder was ultrasonically dispersed in ethanol using a Model JY92-2D Ultrasonic Cell Crusher to produce a well-dispersed SiO_2-alcohol suspension. The suspension was then added to the Si powder and further mixed for 30 min, resulting in a well-dispersed Si-SiO_2 mixture. Afterwards, the phenolic resin powder and the dried Si-SiO_2 mixture were blended for 30 min using a QM-3SP4 ball-milling machine. The final mixtures were heated at 1400 °C for 3 h in a small corundum crucible with a corundum lid, which was embedded in a larger closed corundum crucible filled with graphite powder.

2.3. Characterization

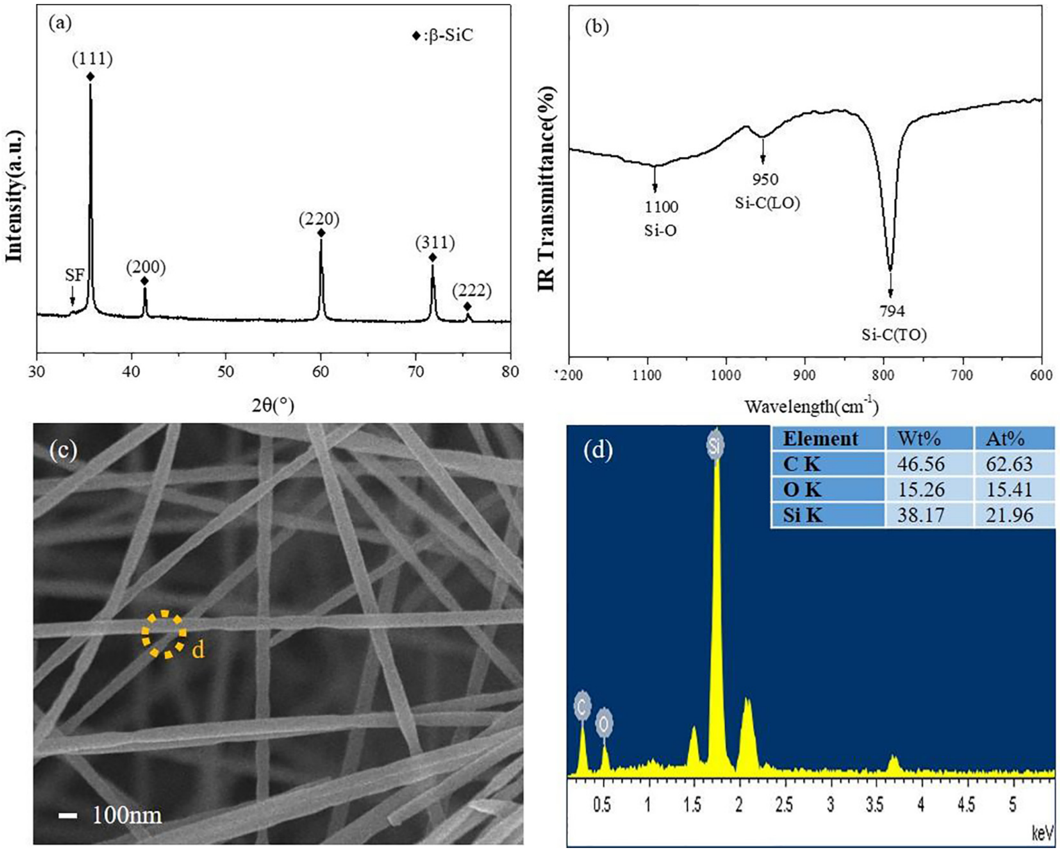
The phase composition of the obtained products was identified by X-ray diffraction (XRD, Cu Kα, 40 kV, 30 mA, Philips X'pert). The microstructure of the samples was investigated by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-700F, Japan) and (high-resolution) transmission electron microscopy ((HR) TEM, JEOL, JEM-2100). Fourier-transform infrared (FT-IR) and photoluminescence (PL) spectra were measured at room temperature using a Bruker, Tensor Ⅱ spectrophotometer within the range of 350–1200 cm^{-1} and a fluorescence spectrophotometer (Fluorolog, Horiba, Jobin Yvon) with Xe lamp excitation.

3. Results and discussion

The XRD pattern of the fabricated SiC NWs (Fig. 1a) shows five major diffraction peaks that can be indexed as the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) crystal planes of β-SiC, with a lattice parameter of α = 4.3589 Å (JCPDS Card no. 29–1129). No other phase was observed, indicating that the as-synthesized products were pure SiC crystal. The FT-IR spectrum is shown in Fig. 1b. The absorption peak at 794 cm^{-1} is the transversal optic (TO) Si-C stretching vibration, and the peak at 950 cm^{-1} attributes to the longitudinal optic (LO) vibration [11]. The relatively weak band from the Si-O stretching vibration (1000 cm^{-1}) indicates the existence of amorphous SiO_2 [12].

As shown in Fig. 1c, the obtained β-SiC NWs have different morphologies, including linear, chain-bead, and bamboo-shaped, and their lengths range from 10 to 100 μm with diameters between 80 and 650 nm. EDS analysis (Fig. 1d) confirmed that the surface of the β-SiC NWs (marked in Fig. 1c) mainly comprised C and Si and a small amount of O, indicating that amorphous SiO_2 exists on the surface. Furthermore, there were no liquid droplets on the tips of the NWs, indicating a typical vapour-solid growth mechanism.

The detailed microstructure of the SiC NWs was further characterized by TEM and HRTEM. As shown in Fig. 2, the NWs have different morphologies (chain-bead, bamboo-shaped, and linear), which conforms to the SEM image in Fig. 1c. In the chain-bead morphology (Fig. 2b), SiC beads with diameters of 460–650 nm are situated within a chain with a diameter of 150–200 nm. Similarly, the bamboo-shaped SiC NWs (Fig. 2c) have alternating stems and nodes along the growth direction of the NW, with diameters of about 150 and 80 nm, respectively. In contrast, the linear β-SiC NWs (Fig. 2d) show no significant fluctuation in diameter, with a diameter of 240 nm. Fig. 2e shows the corresponding SAED pattern of the rectangular area in Fig. 2d, which can be indexed to β-SiC. The HRTEM image in Fig. 2f confirms a uniform interplanar spacing of 0.25 nm with a perfect crystal structure. This is well matched with the (1 1 1) lattice, indicating that these β-SiC NWs grow along the [1 1 1] direction. There are some stacking faults in the linear



Element	Wt%	At%
C K	46.56	62.63
O K	15.26	15.41
Si K	38.17	21.96

Fig. 1. (a) XRD pattern, (b) FT-IR absorption spectrum, (c) SEM image, and (d) EDS spectrum of SiC NWs.