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Synthesis of several millimeters long SiC–SiO_2 nanowires by a catalyst-free technique

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ABSTRACT

In situ synthesis of ultra-long SiC–SiO_2 nanowires were successfully conducted with the raw materials of silicon and phenolic resin by an effective and catalyst-free technique. Several millimeters long SiC–SiO_2 nanowires with the diameters in the range of 50–200 nm were mainly composed of Si, C and a small amount of O, and the formation of several millimeters long SiC–SiO_2 nanowires was attributed to a low flow rate and carbon sources supplied continuously by the pyrolysis of phenolic resin. A catalyst-free vapor–solid (VS) growth mechanism was proposed to illustrate the growth process of ultra-long SiC–SiO_2 nanowires in present experiment, which provides a promising method for in situ fabrication of SiC–SiO_2 nanowires as reinforcements into composites.

1. Introduction

SiC as one of the most widely used non-oxide ceramics has many excellent properties (i.e., high thermal stability, good mechanical behavior and chemical inertness), which make it can be operated at high power and temperature, and under harsh environments [1–5]. In addition to owning the above properties, one dimensional (1-D) SiC nanomaterials (i.e., nanowires and nanorods) exhibit unique mechanical, electrical and optical properties, and show fruitful potential applications in composites and nanodevices [6–8]. Among these 1-D nanostructures, SiC nanowires have attracted considerable interest because of their potential applications in nanocomposites, microelectronic, and nanodevices [9,10]. According to the recent delicate measurement by Wong et al. using atomic force microscopy and lithography techniques, the yield strength of SiC nanowires is over 50 GPa indicating that it has great potential in composite as reinforcement with high strength and toughness [11,12]. However, to the best of our knowledge, the excellent reinforcement efficiency of SiC nanowires in composites was rarely reported. The critical challenges of improving the reinforcement efficiency of SiC nanowires in composites are the way of introducing SiC nanowires into the composites (i.e., the content and distribution of SiC nanowires) and the interface between nanowires and the matrix [12]. According to the previous literature with high reinforcement efficiency of SiC nanowires into SiC matrix by Wen Yang in 2005, in situ process provides a promising solution to improve the reinforcement efficiency of SiC nanowires in composites [12]. Furthermore, ultra-long SiC nanowires (the lengths up to several millimeters or even centimeters) may be more suitable to study the properties of nanostructures on a macroscopic scale compared with the short ones [13–17], which could open up a new opportunity in the application of integrated nanoelectronics and nanocomposites. In addition, a simple and effective way of in situ preparation of ultra-long SiC nanowires is still needed to develop.

This paper attempts to adopt an effective and low-cost method for in situ synthesis of several millimeters long SiC nanowires, in which phenolic resin and silicon powder were chosen as the raw materials. Although similar results have been reported [18], the novelty of this paper is to show the in situ formation of several millimeters long SiC–SiO_2 nanowires with remarkably different growth model compared with previous literature. This way has inherent advantages with an effective and simple procedure, which provides a promising approach to in situ fabrication of ultra-long SiC–SiO_2 nanowires in composites with excellent properties [19–21].

2. Experimental

2.1. In situ preparation of several millimeters long nanowires

Commercial phenolic resin and silicon were used as raw materials to synthesize several millimeters long SiC nanowires. A detailed synthesis process was described as follows. Firstly, the yield of the resin carbon was about 44.2 wt% as shown in Fig. 1 according to the thermogravimetry curve of phenolic resin. Based

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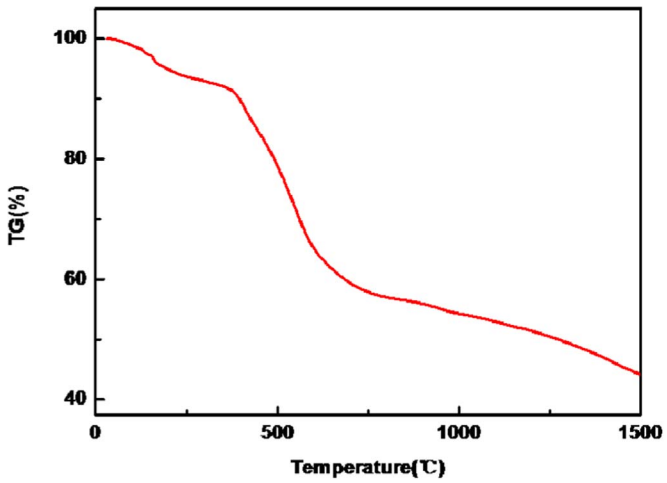

Fig. 1. Thermogravimetry curve of phenolic resin in Ar atmosphere.

on the yield of the resin carbon, the mass ratio of phenolic resin to silicon was calculated, in which the mole ratio of carbon to silicon was kept at 1.67:1. The composite-powder, including phenolic resin and silicon, were homogeneously mixed by a high frequency mixer for 30 min and placed into a ceramic crucible, and then the crucible was sent into a tube corundum furnace. The argon gas (99.999%) was introduced into the furnace at a flow rate of 200 ml/min for ten minutes and then changed the flowing speed to 70 ml/min before heating, while the argon was kept flowing during the experimental process. The furnace was heated up to 200 °C by 40 min and maintained for 10 min, and heated up to 800 °C at 5 °C/min and maintained for 120 min, and then heated up to 1300–1400 °C at 5 °C/min and maintained for 2 h. After the heating was terminated, the furnace was cooled to 500 °C with 5 °C/min and then naturally cooled to room temperature. Finally, the white cotton–wool products were both obtained on the surface of composite-powder, namely in situ growth, and the inner walls of ceramic crucible.

2.2. Characterization

The phase identification and chemical composition of the white wools were analyzed by X-ray diffraction (XRD, X'PERT PRO MPD, Holland). Scanning electron microscopy (SEM, HELIOS NanoLab 600i, America) equipped with energy dispersive spectroscopy (EDX) was used to observe the morphology and analyze the elemental composition of the obtained products. Transmission electron microscopy and high-resolution transmission electron microscopy (TEM and HRTEM, Tecnai G^2-F30, America) were used to identify the microstructure of the samples. Fourier transform infrared spectroscopy (FTIR, Spectrum Two, America) was also conducted to confirm the composition of the product.

3. Results and discussion

3.1. Pyrolysis process of phenolic resins

The pyrolysis process of phenolic resins played an important role in the preparation of several millimeters long SiC–SiO_2 nanowires, and the thermogravimetry (TG) curve in an inert atmosphere with a heating rate of 10 °C/min was used to investigate the pyrolysis process of phenolic resin as shown in Fig. 1. It can be seen that the complete pyrolysis temperature of phenolic resin was about 1500 °C, and the TG curve included three temperature ranges of apparent weight loss. The first one was from room temperature to 140 °C due to the elimination of water and residual solvent in phenolic resin [22], and the second one was from 300 to 600 °C caused by the release of different gases generated by the decomposition of phenolic resin, which includes CO, CH_4 and H_2. H_2 was the dominant product evolved during the third stage (from 900 to 1500 °C) and to form a carbonaceous char [22,23].

3.2. Preparation and characterization of several millimeters long nanowires

A suitable preparation temperature as one of the most important process parameters should be selected carefully to synthesize ultra-long SiC nanowires, which has been studied frequently, and the photographs of products obtained at different preparation temperatures and holding times are shown in Fig. 2 [24]. At 1300 °C for 2 h, almost no obvious white cotton–wool products were found suggesting that the nanowires could not be greatly produced below or even at this temperature (Fig. 2a). The surface of composite-powder and the inner walls of ceramic

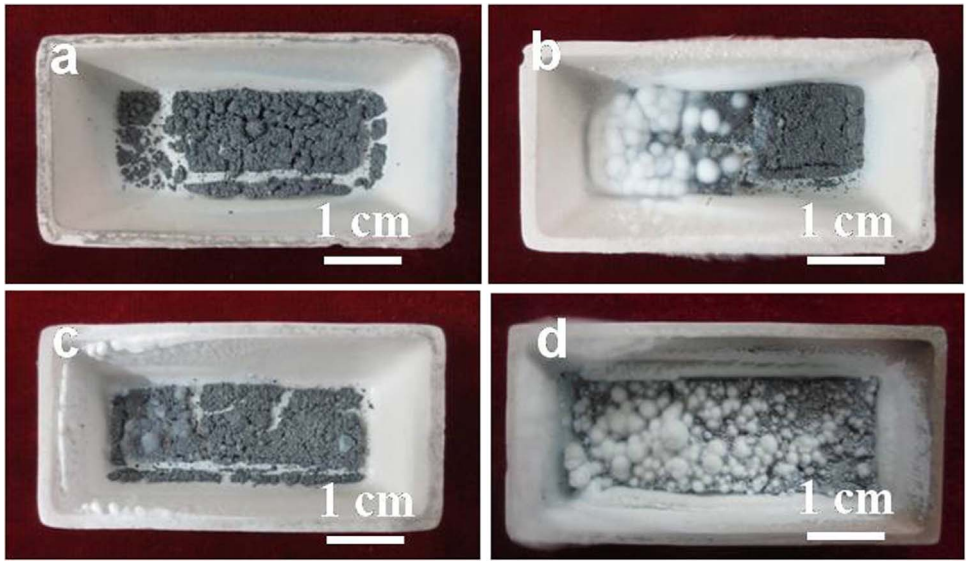

Fig. 2. Photographs of as-prepared products obtained at different preparation temperatures and holding times. (a) at 1300 °C for 2 h, (b) at 1350 °C 2 h, (c) at 1400 °C 2 h and (d) at 1350 °C for 4 h.