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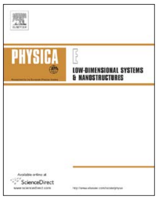

Large scale synthesis of α-Si_3N_4 nanowires through a kinetically favored chemical vapour deposition process

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ABSTRACT

Understanding the kinetic barrier and driving force for crystal nucleation and growth is decisive for the synthesis of nanowires with controllable yield and morphology. In this research, we developed an effective reaction system to synthesize very large scale α-Si_3N_4 nanowires (hundreds of milligrams) and carried out a comparative study to characterize the kinetic influence of gas precursor supersaturation and liquid metal catalyst. The phase composition, morphology, microstructure and photoluminescence properties of the as-synthesized products were characterized by X-ray diffraction, fourier-transform infrared spectroscopy, field emission scanning electron microscopy, transmission electron microscopy and room temperature photoluminescence measurement. The yield of the products not only relates to the reaction temperature (thermodynamic condition) but also to the distribution of gas precursors (kinetic condition). As revealed in this research, by controlling the gas diffusion process, the yield of the nanowire products could be greatly improved. The experimental results indicate that the supersaturation is the dominant factor in the as-designed system rather than the catalyst. With excellent non-flammability and high thermal stability, the large scale α-Si_3N_4 products would have potential applications to the improvement of strength of high temperature ceramic composites. The photoluminescence spectrum of the α-Si_3N_4 shows a blue shift which could be valued for future applications in blue-green emitting devices. There is no doubt that the large scale products are the base of these applications.

1. Introduction

Inorganic nanowires have been the emphasis of recent researches due to their potential application as an active element or interconnect in manufacturing electronic or photonic devices, batteries, supercapacitors, nanocomposites and so on [1–6]. Extensive efforts have been made in the preparation of nanowires with various compositions by using solution-based [7], gas-based [8], template [9] or other methods. Yet to go forward existing applications of inorganic nanowires will require the progress of techniques that enable sufficient scale and high quality of nanowire products.

Silicon nitride (Si_3N_4), an important semiconductive and high-temperature material with several applications in optoelectronic devices and nanowire reinforced ceramics, can form single crystalline nanowires or nanobelts [10–12]. As Si_3N_4 is one of the most important nonoxide inorganic high-temperature and semiconductive material, have vital applications for nanofiber reinforced composites and optoelectronic devices, the synthesis of Si_3N_4 one dimension (1D) nanostructures have been rapidly developed [13–15]. For example, Weiyou Yang et al. [15] synthesized single crystalline α-Si_3N_4 nanowires via thermal decomposition of a polysilazane preceramic polymer using $FeCl_2$ powders as catalysts. Juntong Huang *et al.* [11] prepared α-Si_3N_4 nanowires on a graphitic felt via a Ni-catalyzed chemical vapour deposition (CVD) process. However, it is difficult to separate metal catalysts from the products prepared by the above stated methods, and furthermore, their yield is low relatively.

CVD is an important vapour-based method in preparing of Si_3N_4 1D nanostructures. Based on an appropriate thermodynamically condition, the major kinetic barrier in synthesizing Si_3N_4 nanowires is the supersaturation of the precursor gases. As Younan Xia et al. [16] reported, in principle, it is possible to process any solid material into 1D nanostructures by controlling the supersaturation at a relatively low level. For this reason, theoretically, it is possible to improve the yield of the nanowire products by controlling the supersaturation of the precursor gases at the substrate area.

As reported, lots of papers discussed the effect of temperature to the

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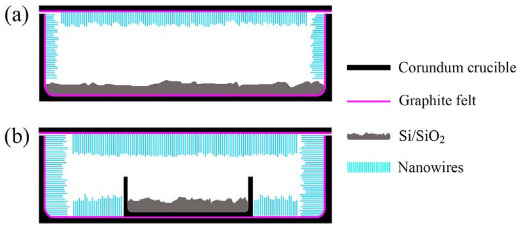

Scheme 1. Schematic experimental setup for Si_3N_4 nanowire synthesis.

yield, morphology, and phase composition of the one dimensional nanostructure products [17–19]. Nevertheless, there are few papers discussing the effect of kinetic factors to the products. Here we report a vapour-based approach, in which process two simple reaction systems were designed in order to discover the effect of gas distribution to the yield of products. A large scale of nanowire products could be prepared by the modified process. The effect of precursor supersaturation, nanowire growth kinetics, and possible gas transportation are studied. Photoluminescence of the as-prepared nanowires is also characterized. This study is of significance for the controlling growth of α-Si_3N_4 nanowires in very large scale and their effective application.

2. Experimental

2.1. Preparation of α-Si_3N_4 nanowires

The synthesis of α-Si_3N_4 nanowires was carried out in a high-temperature vacuum furnace via a chemical vapour deposition method. In order to investigate the influence of gas diffusion and distribution to the yield of the nanowire products, two facile and simple equipment was used as the reactor as shown in Scheme 1. In a typical procedure, Si and SiO_2 (α-quartz) were used as raw material powders and milling in a ball mill (~5 h) with a molar ratio of 1:1. To guarantee the continuous generated of precursor gases during the whole reaction process, 5 g milled composite powder was loaded in the corundum boat. For Route A, the composite powder was loaded into a 100 mm × 60 mm × 30 mm (length × wide × height) corundum boat directly (the inner wall of the corundum boat was paved cleaned graphite felt), as shown in Scheme 1a. For Route B, 5 g composite powder were loaded into a smaller corundum boat (60 mm×30 mm×15 mm) placed in the center of a larger corundum boat as above mentioned, as shown in Scheme 1b. Gas diffusion and distribution control in the process of the reaction was realized by the above mentioned facile equipment. The as-designed reactors were placed in the center of the vacuum furnace. Then the furnace was evacuated to ~10 Pa and aerated to 0.14 MPa by the inlet of nitrogen gas (purity 99.999% (v/ v)). The furnace was then heated from room temperature to 1000 °C at 10 °C/min, to 1450 °C at 3 °C/min and held for 3 h. After cooling to room temperature, the white colored cotton-like products were collected.

2.2. Characterization

The phase composition, morphology, and microstructure of the as-collected products were then characterized using X-ray powder diffraction (XRD, D/max-rA, Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation (λ = 1.54178 Å), field emission scanning electron microscope (FESEM, JEOL JSM6700F, Japan), transmission electron microscopy (TEM/HRTEM, FEI-Tecnai-G^2-F20, Philips, Netherlands) combined with energy-dispersive X-ray spectroscopy(EDS). Thermal gravity analysis (TGA Q5000, TA Instruments, US) was carried out from 25 to 1400 °C at a heating rate of 10 °C/min and maintained at 1400 °C for 30 min. The yield of the as-prepared products from these two different routes was weighed by an automatic analytical balance and photographed by a digital camera. The room temperature photoluminescence (PL) measurement was conducted using a fluorescence spectrophotometer (Hitachi F-4600, Japan) under the excitation of a 254 nm Xe lamp.

3. Results and discussion

Chemical vapour deposition (CVD) is an important bottom-up process in the synthesis of 1D nanostructures [8,10]. In a typical CVD process, the as-prepared product is usually a thermodynamically favored one. However, in these processes, as reported, anisotropic growth usually kinetically governed by supersaturation or through the use of a catalyst [16]. Anisotropic growth products could be achieved by controlling the supersaturation at a low stage. A medium supersaturation state is beneficial to the growth of the bulk crystals. At high supersaturation, nuclei are uniformly generated in vapour phase and form powder products. Therefore, it is crucial to control gas distribution (which relates to the variation of supersaturation) in the CVD processes.

Silicon nitride (Si_3N_4) is an important wide band-gap semiconductor (5.3 eV). In recent years, researchers synthesized 1D Si_3N_4 nanostructures via vapour based methods including vapour-liquid-solid mechanism and vapour-solid mechanism. In a typical CVD process, due to the use of relatively high temperatures, the detailed mechanism may include the generation of various intermediates or precursors. In preparing Si_3N_4 nanowires, the vapour phases silicon monoxide (SiO), Si and Si_xO ($x > 1$) seems to be key intermediates [10,11,14,16]. For that reason, the yield of 1D Si_3N_4 nanowires could be controlled by adjusting the distribution of these vapour intermediates.

In this research, a low-cost composite powder mixture (Si/SiO_2) was used as the raw material. Fig. 1 shows the thermal gravity analysis (TGA) of the raw powder. The temperature was increased to 1400 °C at

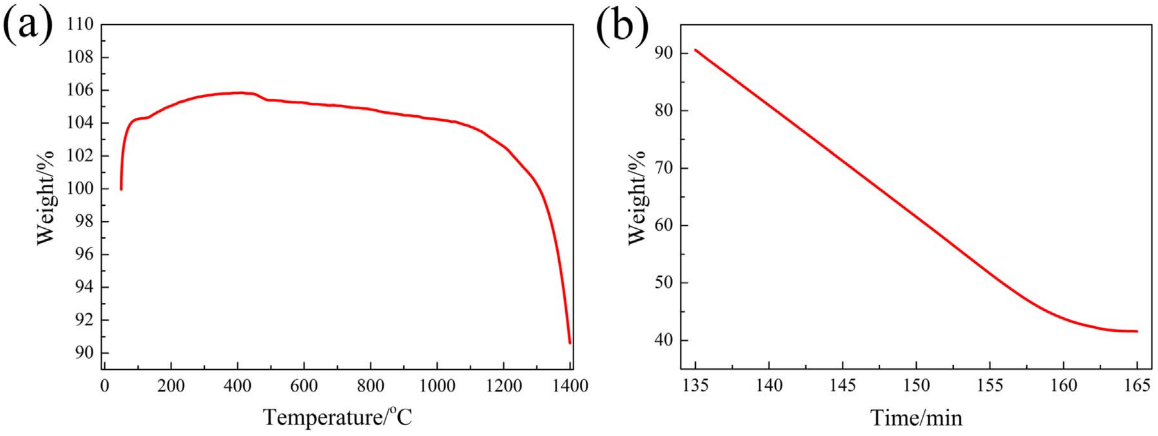

Fig. 1. The TGA curve of Si/SiO_2 powder mixtures using flowing Ar as gas carrier. The temperature increased from room temperature to 1400 °C (a) and maintained for 30 min (b).