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Low temperature formation of AlN nanofibers by carbothermal reduction nitridation of hydrothermal precursor fibers

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ABSTRACT

AlN nanofibers were fabricated by carbothermal reduction (CRN) method of hydrothermal precursor fibers using aluminum nitrate, urea, glucose and polyethylene glycol as raw materials. The as-fabricated samples were characterized by TG-DSC, XRD, SEM, EDS, and UV–vis absorption and PL spectra. The results indicated that raw materials were transformed to $NH_4Al[(OOH)HCO_3]$ (AACH) fibers in hydrothermal process, carbon coated γ-Al_2O_3 fibers in decomposition process, and AlN nanofibers in CRN process. In relation to other CRN methods, the hydrothermal precursors reduced the fabrication temperature in 200 °C. The diameter of the AlN nanofibers fabricated at 1400 °C was 90–110 nm with several micrometers length. These fibers showed broad absorption band from 190 to 230 nm with an absorption edge at 198 nm and obvious emission at approximately 478 nm and 577 nm excited by 350 nm, indicating a valuable application in light-emitting nanodevices. Such a strategy can be extended to synthesize other nitride fibers.

1. Introduction

In the past couple of decades, much research has been done on the synthesis and characterization of AlN semiconductor nanostructures, due to its novel properties, including high thermal conductivity, excellent optical and dielectric properties, low dielectric constant and good mechanical strength [1–3]. AlN nanofiber is one of these materials, having a wide range of application such as field-emission [4], flexible pulse-wave sensors [5], and optoelectronic industries [6].

Various synthetic routes including self-assembly [7,8], liquid-vapor-solid (LVS) method [9–11], self-propagating high-temperature synthesis (SHS) [12,13] and carbothermal reduction nitridation (CRN) [14–16] have been developed to fabricate AlN nanofibers. Compared with other synthetic methods, the fabricated technique of CRN is suitable for generating nanofibers with exceptional length and processes the virtues including simplicity, low cost and absence of high voltage. However, in CRN methods, the fabrication temperature is usually 1600 °C or higher. Sun et al. [14] fabricated AlN hollow fibers by electrospun precursor of Al_2O_3 fibers and C powders at 1600 °C for 5 h in N_2 atmosphere. Yin et al. [16] fabricated single-crystalline AlN nanotubes with carbon-layer coatings on the outer and inner surfaces via a multiwalled carbon nanotube template induced route at 1600 °C for 1 h in ammonia atmosphere with a flow of 200 sccm. Therefore, an improvement and low nitridation temperature CRN method is needed. In addition, rare researchers have investigated the optical properties of AlN nanofibers.

In this work, AlN nanofibers were fabricated at 1400 °C, which is 200 °C lower than previous researches. The fabrication mechanism and optical properties have been investigated and interpreted.

2. Experimental

2.1. AlN nanofibers synthesis

Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, Aladdin, AR), polyethylene glycol (PEG, $HO(CH_2CH_2O)_nH$, Mn = 1000, Aladdin, AR), urea (NH_2CONH_2, Aladdin, AR) and glucose ($C_6H_{12}O_6{\cdot}H_2O$, Aladdin, AR) were used as the raw materials.

Firstly, a clear solution was prepared by dissolving 16 g of polyethylene glycol into 35 mL deionized water, and then 8 g aluminum nitrate, 3.52 g glucose and 20 g urea were added into the solution. After completely dissolving, 70 mL mixed solution was added into 100 mL capacity teflon-lined autoclave. The autoclave was sealed

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and maintained at 120 °C constantly for 24 h and then cooled to room temperature naturally. Hydrothermal products were dried in electric drying oven at 80 °C for 12 h without centrifuging and washing. After drying, hydrothermal products were calcined under nitrogen atmosphere at 900 °C for 1 h, and precursors of carbon coated gamma alumina fibers were obtained.

Secondly, precursors were heated at 1300, 1400, 1500 and 1600 °C for 2 h under flowing N_2 atmosphere; residual carbon in each nitridation product was removed by firing under air atmosphere at 700 °C for 2 h. And AlN nanofibers were fabricated.

2.2. Characterization of AlN nanofibers

Thermal and X-ray diffraction analysis were performed on differential scanning calorimeter and thermal gravimeter (TG-DSC, SQT-600, TA Instruments) and X-ray powder Diffract (XRD, D2 PHASER, BRUKER) using Cu Kα radiation, respectively. Morphologies were measured by scanning electron microscope (SEM, HITACHI SU-8010). Surface concentrations were measured by an energy dispersive X-ray spectroscope (EDS, TEAM Apollo XL, EDAX) using the unit attached to the SEM. Optical absorption was investigated by the UV–vis absorption spectroscopy (UV 3600, SHIMADZU). Photoluminescence spectrum (PL) at room temperature was measured by spectrophotometer (FL3-211, HORIBA Jobin Yvon) with InGaAs as detector in 400–650 nm wavelength regions using an argon ion laser as the excitation source (350 nm).

3. Results and discussion

3.1. Sample characterization

The TG-DSC curves of hydrothermal products are shown in Fig. 1. The weight loss of about 10% in the range of 50–100 °C was attributed to the evaporation of moisture. At 225 °C, the evident exothermic peak accompanied with 35% weight loss was due to the decomposition of aluminum basic salts. Between 286 and 416 °C, the 45% weight loss was originated from decomposition of polyethylene glycol and carbonization of glucose. There was no weight loss above 600 °C, which suggested that aluminum basic salts, polyethylene glycol and glucose were decomposed completely. And the absence of DSC peaks between 600 and 1000 °C revealed no crystal transformation in this temperature range.

Fig. 2(a) and (b) shows XRD patterns of hydrothermal products and precursors, respectively. No peaks were confirmed, seeming both of them were amorphous state. However, in our opinion, there must be same amorphous carbon layers coating on them, therefore

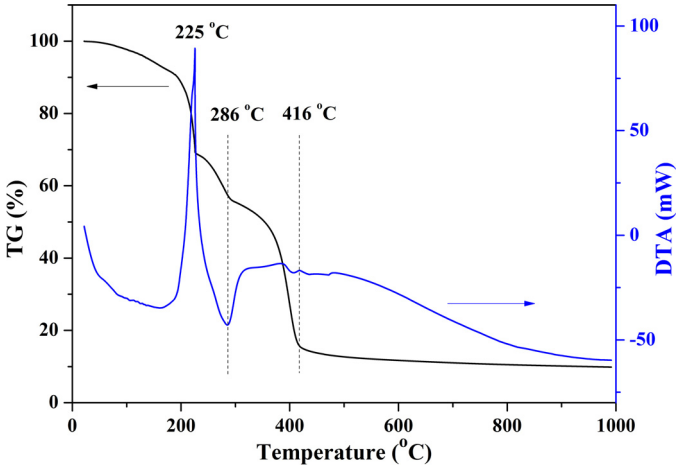

Fig. 1. TG-DSC curves of hydrothermal products.

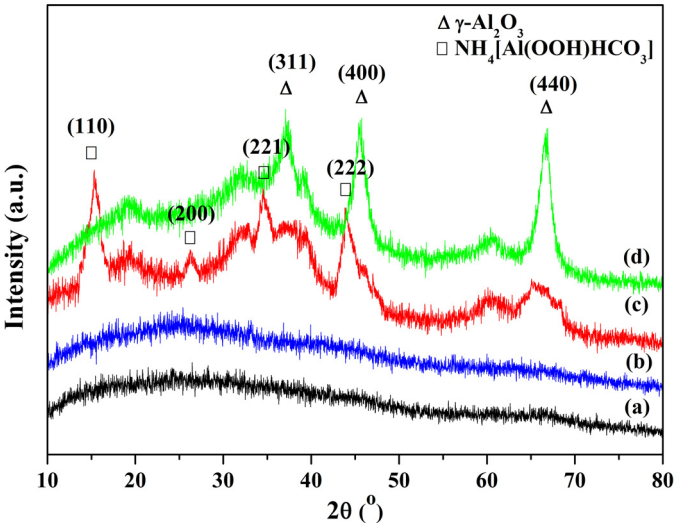

Fig. 2. XRD patterns of hydrothermal products and precursors (a, hydrothermal products; b, precursors; c, hydrothermal powders without carbon; d, precursors without carbon).

resulting in no obvious peaks in the XRD patterns. In order to prove this claim, samples were calcined in the air at 200 °C for 24 h to remove the carbon. And the XRD patterns of calcined powders were shown in Fig. 2(c) and (d), respectively. As shown in Fig. 2(c), the diffraction peaks associated with ammonium aluminum carbonate hydroxide ($NH_4Al[(OOH)HCO_3]$, denoted as AACH, JCPDS: 42-0250) were observed, indicating the hydrothermal products were amorphous carbon coated AACH. Similarly, Fig. 2(d) indicated that the precursors were amorphous carbon coated gamma alumina (γ-Al_2O_3, JCPDS: 50-0741).

SEM images and EDS patterns of hydrothermal products and precursors are shown in Fig. 3. It could be observed that the hydrothermal products were fibers with diameter of 120–150 nm and length of several micrometers, as shown in Fig. 3(a). Furthermore, a rough layer could be observed on the surface of these fibers in the inset image of Fig. 3(a). Meanwhile, the corresponding EDS pattern of these fibers showed that the fibers were composed of Al, O, N and C, as shown in Fig. 3(b). While, as seen in Fig. 3(c), although there was no obvious difference in the diameter and length between precursors and hydrothermal products at low magnification, 10–20 nm powders could also be seen on the surface of precursors, as shown in the inset image of Fig. 3(c). The corresponding EDS pattern of these fibers shows only Al, O and C. These results further confirmed that hydrothermal products and precursors were carbon coated AACH fibers and carbon coated γ-Al_2O_3 fibers, respectively.

Fig. 4 shows the XRD patterns of the AlN fibers fabricated at 1300, 1400, 1500 and 1600 °C. As shown in Fig. 4(a), AlN (JCPDS: 65-3049) and γ-Al_2O_3 (JCPDS: 50-0741) phases co-existed in the fibers at 1300 °C. However, only AlN phase was detected in the AlN fibers fabricated at 1400 °C or higher, as shown in Fig. 4(b)–(d), and the diffraction peaks became sharper and narrow with the increase of temperature. The results showed that from hydrothermal precursors, the fabrication temperature of AlN fibers by carbothermal reduction and nitridation method could decrease to as low as 1400 °C. Compared to other precursors [14,16], the fabrication temperature was about 200 °C lower.

Fig. 5 shows the SEM images of the AlN fibers fabricated at 1300, 1400, 1500 and 1600 °C, and the EDS pattern of AlN fibers fabricated at 1400 °C. As shown in Fig. 5(a), the diameters of the AlN fibers fabricated at 1300 °C were 80–100 nm and the lengths were several micrometers. Compared to the precursors, as shown in

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