Fabrication of aluminum nitride (AlN) hollow fibers by carbothermal reduction and nitridation of electrospun precursor fibers

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The fibers of AlN were synthesized by carbothermal reduction and nitridation of precursor fibers obtained by electrospinning. XRD result indicated that the wurtzite AlN phase had been successfully synthesized in fibers. The SEM and TEM analysis indicated that the hollow fibers with an outer diameter of about 500 nm and a wall thickness of about 100 nm were obtained and the crystal in fibers was hexagonal after calcination. The fibers were further characterized by TG–DTA, FT-IR and UV–vis absorption spectra. The formation mechanism of hollow structure was proposed based on our understanding and characterizations.

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1. Introduction

Over the past decade, one-dimensional ceramic fibers have become the focus of scientific research due to their exceptional properties and novel potential applications in many fields [1–3]. A large number of fabrication methods including chemical vapor deposition (CVD) [4], hydrothermal reduction method [5], template synthesis [6], electrospinning [7] and other methods have already been demonstrated for generating fibers materials. Among these methods, as a simple and versatile technique, electrospinning has been widely deployed for the fabrication of polymer nanofibers with exceptional length, uniform diameter, and diversified compositions [8,9]. Moreover, ceramic fibers can also be prepared by calcination of electrospinning mixture solutions of ceramic precursors and polymers.

One-dimensional III–V semiconductor nanostructures are attracting great interest for their promising high impact in optoelectronics applications, such as optoelectronic devices in the UV and visible region. AlN is an important wide-band gap semiconductor due to their large band gap of ∼6.2 eV [10]. With high thermal stability (up to 3000 K), low or even negative electron affinity, piezoelectric capabilities [11–13] AlN nanofibers appear to be promising for a wide range of applications such as field-emission applications and flexible pulse-wave sensors [14–16]. Based on the excellent physical properties, such as high thermal conductivity, high electrical resistivity and a weak thermal expansion coefficient close to Si, AlN is suitable for applications including high-temperature and high-power devices, frequency ultrasonic transducers, acoustic wave sensors, optoelectronic devices and microelectronic substrate [17–19].

Various synthetic routes including self-assembly, liquid–vapor–solid (LVS) method and self-propagating high-temperature synthesis (SHS) have been developed to fabricate AlN nanofibers. In this paper, AlN hollow nanofibers could be prepared by high-temperature carbothermal reduction and nitridation of electrospun composite fibers. Compared with the other synthetic methods, the fabricated technique used in this work is suitable for generating nanofibers with exceptional length and processes the virtues including simplicity, low cost and absence of template [20–21].

2. Experimental details

Al(NO₃)₃·9H₂O supplied by Tianjin Kermel Chemical Reagent Ltd. and urea obtained from Shenyang Xinxing Chemical Reagent Ltd. were used as starting material to synthesize AlN fibers. For achieving composite solution, the 13.7300 g Al(NO₃)₃·9H₂O and 1.0989 g urea were dissolved into 8 ml solvent containing 5 ml de-ionized water and 3 ml absolute alcohol, followed by the addition of 6 g poly(vinyl pyrrolidone) (PVP, K30) (Sinopharm Chemical Reagent Co. Ltd.) to increase viscosity. Subsequently, the mixed solution was magnetically stirred for 2 h at room temperature to form a homogeneous viscous solution. The composite solution was then drawn into a plastic syringe with a stainless steel needle, which was connected with high-
voltage power supply and used as the spinneret. The angle between and the fixing bar was about 45° and the distance between needle and the grounded collector was about 15 cm. A voltage of 30 kV was supplied to the solution to allow the formation of a sprayed dense net of fibers deposited on the collector.

For comparing, the precursor fibers without the addition of urea were also obtained by electrospinning. The precursor fiber mat was dried at 100°C for 3 h, and then heated up to 1600°C for 5 h in three stages as schedule shown in Fig. 1. First stage, the precursor fibers were carbonized at 500°C for 1 h in vacuum. With the increasing of temperature to 1000°C, the N2 was provided as nitrogen source and carbon was used as the reducing agent. Subsequently, these fibers were heated at 1300, 1400 and 1600°C for 5 h for carbothermal reduction and nitridation.

Thermal gravimetry–differential thermal analysis (TG–DTA) was performed on a thermoanalyzer (Mettler, TGA/SDTA851) from 50 to 700°C in N2 atmosphere and X-ray diffraction patterns (XRD) were collected on a Shimadzu/XRD-6000 diffractometer with Cu Kα radiation. JSM-5600LV scanning electron microscopy (SEM, JEOL) and Tecnai G220 S-Twin transmission electron microscopy (TEM, FEI) were used to characterize the morphology of the fiber. The optical properties were investigated by the UV–vis absorption spectroscopy (UV-550, Jasco) and Fourier transformed infrared (FT-IR) spectroscopy (EQUINOX55, Bruker).

3. Results and discussion

The thermal behaviour of the precursor fibers under flowing nitrogen is shown in Fig. 2. There is no weight loss above 600°C because organic materials (PVP, absolute alcohol), urea, nitrate and volatiles (H2O, COx, etc.) were decomposed completely. The weight loss of about 10% in the range of 50–200°C could be attributed to the evaporation of moisture and trapped solvent (ethanol) from the precursor. The weight loss in the range of 200–260°C is about 20% due to the decomposition of aluminum nitrate and urea. Between 300 and 500°C, the 40% weight loss is believed to originate from the decomposition and carbonization of PVP. All the exothermic peaks in the DTA curves corresponding to weight losses are broad and weak, implying that the precursor fibers involve slow decomposition and carbonization without the combustion of carbon below 600°C in nitrogen atmosphere.

Fig. 3a shows the XRD pattern of precursor fibers obtained by electrospinning. No peaks were confirmed, indicating the formation of an amorphous state. As shown in Fig. 3b and c, the XRD patterns of the two samples prepared with or without the addition of urea are similar and are consistent with the hexagonal wurtzite AlN phase (JCPDS No. 25-1133) after calcination at 1600°C for 5 h. It is worth noting that the diffraction peaks of products are broadened and shift to the high degree side with the addition of urea, implying that the lattice parameter decreases with the decrease of the AlN grain size. There are no other obvious diffraction peaks in the XRD patterns, which imply that main product is wurtzite AlN phase and no impurity content such as Al2O3 is obtained in fibers. The AlN fibers are formed via the following reaction:

\[ \text{Al}_2\text{O}_3(s) + 3 \text{C}(s) + \text{N}_2(g) \rightarrow 2\text{AlN}(s) + 3\text{CO}(g) \]

The XRD patterns of the fibers at various temperatures are shown in Fig. 4. The AlN crystalline was successfully synthesized.
at 1300 °C. Furthermore, the diffraction peaks of product became sharper and narrow with the increase of temperature, which indicated that the crystallinity was higher and the grain size was larger at high calcinations temperature.

Fig. 5a shows the FT-IR spectra of precursor fibers at room temperature. As shown in IR spectrum, the peaks labeled by number located at 644, 831, 1294, 1654, 2960, and 3432 cm\(^{-1}\) are assigned to the C–OH stretching vibration, CH\(_2\) bending vibrations of PVP, –C stretching of –CH\(_2\) groups, C=O stretching vibration, CH\(_2\) unsymmetrical stretching vibration and O–H stretching vibration of H\(_2\)O, respectively [22–24]. The two peaks around 1360 cm\(^{-1}\) are due to the asymmetric of H–N–H groups, which indicates the presence of ammonium and/or urea derivatives. After calcination at 1600 °C, the spectra (Fig. 5b) show that the organic bands disappeared due to the decomposition of polymer templates. A new broad band around the wave number of 680 cm\(^{-1}\) was found, which corresponded to transverse optical phonon modes of AlN crystal [25]. The other weak peaks can be attributed to a small amount of adsorbed H\(_2\)O, O\(_2\) and CO\(_2\). The absorption peaks of Al–O at 950 or 460 cm\(^{-1}\) [26] could not appear in the FT-IR spectrum, implying no Al\(_2\)O\(_3\) phase existed in fibers.

Fig. 6a shows the SEM images of precursor fibers in the amorphous state. The average diameter of these fibers is about 2 μm and the length could reach several millimeters. The surface of the precursor fibers is very smooth due to the very fine particles or the amorphous nature of the fibers. As shown in Fig. 6b, the fibers calcined at 1600 °C for 5 h looks like a mixture of ribbons and tubes. Which wrinkle or twist in an irregular way. The calcination makes the surface of fibers coarsen and diameter of fibers decreased due to the removal of PVP and crystallization of AlN. The fiber diameters range from 50 to 100 nm. The hollow structure can be observed in the cross-section of the fiber. A quantitative analysis by energy-dispersive spectroscopy (EDS) proves that the components of the product are elements of Al and N and the atomic ratio of Al/N is about 1/1.

The hollow structure of fibers was further characterized by TEM. Fig. 7a clearly shows that the hollow fibers have an out-diameter of about 500 nm and a thin wall thickness of about 100 nm. Most of the fibers were straight with rough surface due to crystallization of AlN. As shown in Fig. 7b, the fibers are composed of hexagonal crystals about 50–100 nm in diameter, which is in accordance with the XRD results. The selected-area electron diffraction (SAED) image (inset of Fig. 7a) which combines partial ring and dot patterns indicates that the fibers have a hexagonal polycrystalline structure. The formation process of this hollow center structure could be described by a mechanism which is similar to that of the spray drying of ceramic powders [27]. As shown in Fig. 7c, with the increase of temperature during the calcination process, PVP becomes viscous and the fiber is plasticized. The trapped solvents (ethanol and water) evaporate and nitrates decompose between 100 and 260 °C.
and the decomposition of PVP between 300 and 500 °C. The gases are released during these processes and the ballooning of the fiber also occurs. If the release rate of gases ($V_r$) inside the fibers is larger than the diffusion rate of gases ($V_d$) through the fiber surface, the pressure inside of the fiber is increased and larger than outside pressure and hollow fibers are formed. This formation mechanism has been discussed in Ref. [28].

The UV–vis absorption spectrum to measure the excitonic or interband transitions of the AlN fibers is investigated here (Fig. 8). The hollow fibers show a broad absorption band from 190 to 230 nm with an absorption edge at 209 nm, corresponding to a band gap of about 6.22 eV. It is in accordance with the highly pure AlN nanobelt [29] and the absorption edge can be well assigned to the optical transition of the first excitonic state of AlN [30–32].

4. Conclusions

The preparation method by electrospinning was used to prepare PVP/Al(NO$_3$)$_3$ precursor fibers in this paper, and hexagonal AlN fibers with hollow structure were successfully synthesized by calcination of as-spun fibers in nitrogen atmosphere at 1600 °C for 5 h. The surface of AlN fibers was rough and the hexagonal crystal of AlN can be clearly observed in fibers. The out-diameter and the wall thickness of hollow fibers are about 500 and 100 nm, respectively. Such a strategy might be extended to the fabrication of other nitride fibers with hollow structure.

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References