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Crystallization and stability of electrospun ribbon- and cylinder-shaped tungsten oxide nanofibers

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Abstract

Tungsten oxide (WO_3) nanofibers with cylindrical (400 ± 200 nm diameter) and ribbon-like (80 ± 10 nm thick ribbons with the width-to-thickness ratio of up to 50:1) shapes were prepared by annealing electrospun polyvinylpyrrolidone/ammonium metatungstate (PVP/AMT) fibers with 1:1 PVP/AMT weight ratio. The effects of annealing temperature (573–1173 K), time (1–12 h), and fibers' shape on their crystalline structure and stability were investigated. Only a polycrystalline monoclinic phase of WO_3 was observed in all experiments, and the grain size increased with temperature and time from a few nanometers to ~1 μm. Results have shown that thermal stability of fibers depend on their shape and whether or not the fibers are clamped to the substrate. Loose fibers of both types were stable to at least 873 K. Ribbon-like structures degraded between 873 K and 973 K, whereas some fraction of cylindrical fibers survived annealing at 1173 K. When both types of fibers were clamped to silicon substrate, annealing above 873 K led to their partial disintegration with the formation of large needle and lamellar WO_3 crystals.

Keywords: Nanofibers; Electrospinning; Tungsten oxide; Crystallization; Microstructure

1. Introduction

Electrospinning has been widely used to manufacture nanofibers of various materials [1–3]. Nearly every electrospinning process involves a polymeric precursor, and inorganic fibers are mostly obtained by thermal decomposition of the polymeric component in fibers containing inorganic salts or other suitable compounds. Oxide nanofibers make the largest group among the electrospun inorganic nanofibrous materials. They include simple and complex oxides for the environmental sensors, enhanced catalysts and catalyst supports, anode materials for lithium batteries, and other uses [2,4–6].

Performance of oxide nanofibers in a particular application depends on their microstructure, chemical and phase composition, shape, surface morphology, porosity, and interconnectivity of individual fibers. Generally, the shape of oxide nanofibers is determined primarily by shape of the original oxide precursor-loaded polymeric fiber, as well as by the annealing conditions. Cylindrical shapes of oxide nanofibers crystallized from electrospun precursor fibers are common, but other fiber shapes, such as belts and ribbons have also been reported for several oxides, for example, In_2O_3/Co_3O_4, Al_2O_3, $BaTiO_3$, $LaFeO_3$, RuO, and Bi_2WO_6 nanofibers [7–12]. A larger surface-to-volume ratio of belt- and ribbon-like nanofibers makes such fiber architectures attractive for numerous applications.

Tungsten trioxide (WO_3) nanofibers have been fabricated via electrospinning process by a number of researchers [13–18]. WO_3 nanofibers demonstrated attractive characteristics in gas sensing [19–24], photocatalytic [25], and electrochromic [26] applications. Fiber crystallinity, grain size, surface morphology and porosity, suitable for such purposes were achieved at the annealing temperatures from 573 K to 973 K, annealing time from 1 h to 8 h, and heating rates from 1 K/min to 10 K/min. Fiber shapes other than cylindrical have not been observed. Most of annealing experiments were conducted with

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loose fibers. Piperno et al. [19] and Ngyen et al. [16] demonstrated the fabrication of sensor structures by crystallizing WO_3 nanofibers directly on the patterned substrate at 573 K and 773 K, respectively.

Evidently, selection of the annealing procedure has been driven by the goal of achieving the best performance of the material for specified usage. Small grain size (20–60 nm) and level of porosity in crystallized WO_3 fiber structures have been viewed as the most influential parameters. Stability of fibers during annealing has also been considered. For example, Kim et al. [24] obtained good fiber structure and gas sensing properties after annealing at 973 K but noted that the fibers cannot maintain their shape above that temperature. Ngyen et al. [16] declared 773 K annealing temperature the best for making WO_3 fiber-based ammonia sensors, whereas Wang et al. [20] stated the same for lower (623–673 K) annealing temperature. The fiber microarchitecture varied significantly from case to case.

Tailoring WO_3 nanofibers shape from cylindrical to ribbon-like could further their application potential. However, the formation of ribbon-like WO_3 fibers using electrospinning and annealing has not been explored. In this study, WO_3 nanofibers with cylindrical and ribbon-like shapes were prepared using a capillary needle dc-electrospinning method. Fiber crystallization behavior and stability during the annealing between 573 K and 1173 K were compared. Experiments showed that WO_3 fibers with different shapes developed similar structure and grain size, but had different porosity and stability at the same annealing temperature. In addition, the fiber stability and crystallization behavior depended on whether or not the fibers were clamped to the substrate. Sections below provide the experimental details and discussion of the results.

2. Experimental

Typical base precursor solution was made by mixing 5.0 mL 30% w/v solution of polyvinylpyrrolidone (PVP, M_w 1,300,000, SigmaAldrich) with 5.0 mL 30% w/v solution of ammonium metatungstate hydrate (AMT, SigmaAldrich) in ultrapure DI water. The resulting 15% w/v PVP/AMT solution with 1:1 PVP to AMT w/w ratio was stirred, sonicated, and aged for 24 h. The concentration of this stock solution was further adjusted within the range from 8% to 15% w/v by diluting with DI water or ethanol in order to modify the fiber diameter and shape.

The dc-electrospinning system included a syringe pump with a 5 mL plastic syringe connected to a 21 gauge capillary needle. The positive electrode of a 40 kV dc-power supply (Gamma High Voltage Research, Ormond Beach, FL) was attached to the needle. The substrates (p-type 10 Ω cm Si (110) wafers) were placed on a grounded stainless steel collector located at a distance of 100–300 mm from the needle. The process was conducted inside a $300 \times 300 \times 300$ mm^3 vented plastic enclosure. The fibers were generated at the flow rate in the range of 0.1–0.25 mL/h, and dc-voltage varied from 15 kV to 25 kV. The process was run for a few minutes to prepare a thin layer of fibers on Si substrate.

The fabricated PVP/AMT precursor fibers were annealed by heating the specimens in the air at a rate of 3 K/min and holding them between 1 and 12 h at the temperatures in the range of 573–1173 K using a programmable furnace (Isotemp 650 from Fisher Scientific).

The size, shape, and surface morphology of the PVP/AMT and resulting WO_3 fibers were investigated with field-emission scanning electron microscopy (FE-SEM, FEI Quanta 650). SEM imaging was done in secondary electron mode, with an accelerating voltage of 15 kV, electron probe current 2 μA, and a chamber pressure of 1×10^{-4} Pa. Chemical composition of the fibers was determined by the electron dispersive spectroscopy (EDS) accessory of SEM. During EDS, the accelerating voltage was 15 kV with an integration time of 300 s.

Transmission Electron Microscopy (TEM) imaging was performed using a JEOL JEM-2100F microscope under an acceleration voltage of 200 kV. The TEM samples of WO_3 fibers were prepared on a formvar-coated nickel grid from an aqueous dispersion of the collected fibers.

Crystalline phase composition was determined using a Philips X'pert MPD thin-film X-ray diffractometer with a Cu Kα tube (wavelength 0.15406 nm, operating at 45 kV and 40 mA) was used to determine the crystalline phase composition. The detector was scanned between 20° and 70° with a constant take off angle of 5°. The experimental diffraction patterns were compared with the ICDD powder diffraction file (PDF) database [27].

MicroRaman spectra were collected from several locations across each sample using Dilor XY microRaman spectroscopy system equipped with a 300 mW solid state laser (Dragon Lasers, Chang Chun, China), operating at $\lambda = 532$ nm and focused to a 10 μm spot size. All measurements were taken in standard laboratory conditions.

3. Results and discussion

Most of electrospinning experiments in this study resulted in a thin layer of randomly oriented intertwined cylindrical PVP/AMT nanofibers with typical diameters in the range of 400–900 nm. Ribbon-like fibers were observed in increasing numbers at higher polymer precursor concentrations. For the PVP/AMT 1:1 w/w precursor and the process conditions used in the experiments, the ribbon-like fiber thickness was typically about 150 nm and rather uniform, whereas the width varied from 1.1 μm to 4.0 μm. The maximum yield ($> 90\%$) of ribbon-shaped fibers was achieved only within a narrow range of the electrospinning process parameters at 15% w/v precursor concentration. A few cylindrically shaped fibers with diameters 650 ± 200 nm were also still present (Fig. 1). The needle-collector distance in the range between 200 mm and 250 mm and voltage between 20 kV and 22 kV played a critical role in achieving the largest yield of ribbon-like structures. The formation of ribbon-like fiber structures has been shown to involve the rapid solvent evaporation and the formation of thin solidified surface layer ("skin") in the propagating polymer jet, followed by evaporation of the residual solvent and then by collapse of the resulting hollow