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PREPARATION AND MORPHOLOGY OF GERMANIUM OXIDE NANOFIBERS

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Abstract. Nanofibers of GeO_2 have been prepared by electrospinning followed by thermal treatment using poly(vinyl acetate) and germanium isopropoxide. The nanofibers have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction method (XRD).

1. INTRODUCTION

Recently, much attention has been paid to the preparation and characterization of one dimensional nanomaterials due to their importance in basic scientific research and potential technology applications [1,2]. Many unique and fascinating properties have been proposed and demonstrated for this class of materials, such as metal-insulator transition [3], superior mechanic toughness [4], higher luminescence efficiency [5,6], enhancement of thermoelectric figure of merit [7] and lowered threshold [8-10]. These nanomaterials can also be used as building blocks to assemble new generations of nano scale electronic circuits and photonics [11-15].

There has been a great deal of interest in obtaining efficient visible luminescence from the indirect gap elemental semiconductors Si or Ge. The structural, optical and electronic properties of low dimensional, indirect band gap materials have been investigated extensively over the past years. Germanium dioxide (GeO_2) is one of the dielectric oxides that are promising materials for optical devices such as optical wave guides for integrated optical systems [16]. GeO_2 nanomaterial is a blue photoluminescence (PL) material, with peak energies around 3.1 eV and 2.2 eV [17], and germanium oxide based glass is thought to be more refractive than the corresponding silicate glass so that the GeO_2 nanomaterials may be used for nanoconnections in future optoelectronic communication. There are several reports on the preparation of one dimensional structures of GeO_2 including GeO_2 whiskers synthesized by laser ablation [18], GeO_2 nanowires prepared via physical evaporation [19], GeO_2 nanorods grown by carbon nanotube confined reactions [20] and thermal oxidation methods [21].

In this work, we report the preparation of GeO_2 nanofibers by an electrospinning method [22-24], an inexpensive technique which is used to prepare the nanofibers with large surface area to volume ratio. We also report the morphology of its nanofibers.

2. EXPERIMENTAL

All the chemicals are used as such and the solvents are purified according to standard methods. Scanning electron microscopy (SEM) images of the products are collected on a JEOL GSM-5900 electron microscope. Atomic force microscope (AFM) pictures are taken using XE-100 (PSIA Co.) instrument. X-ray diffraction (XRD) pattern of the fibers is obtained with Shimadzu Lab-X 600 X-ray diffractometer with Cu-Kα radiation.

The GeO_2 nanofibers have been prepared from germanium isopropoxide ($Ge(OPr^i)_4$) using poly(vinyl

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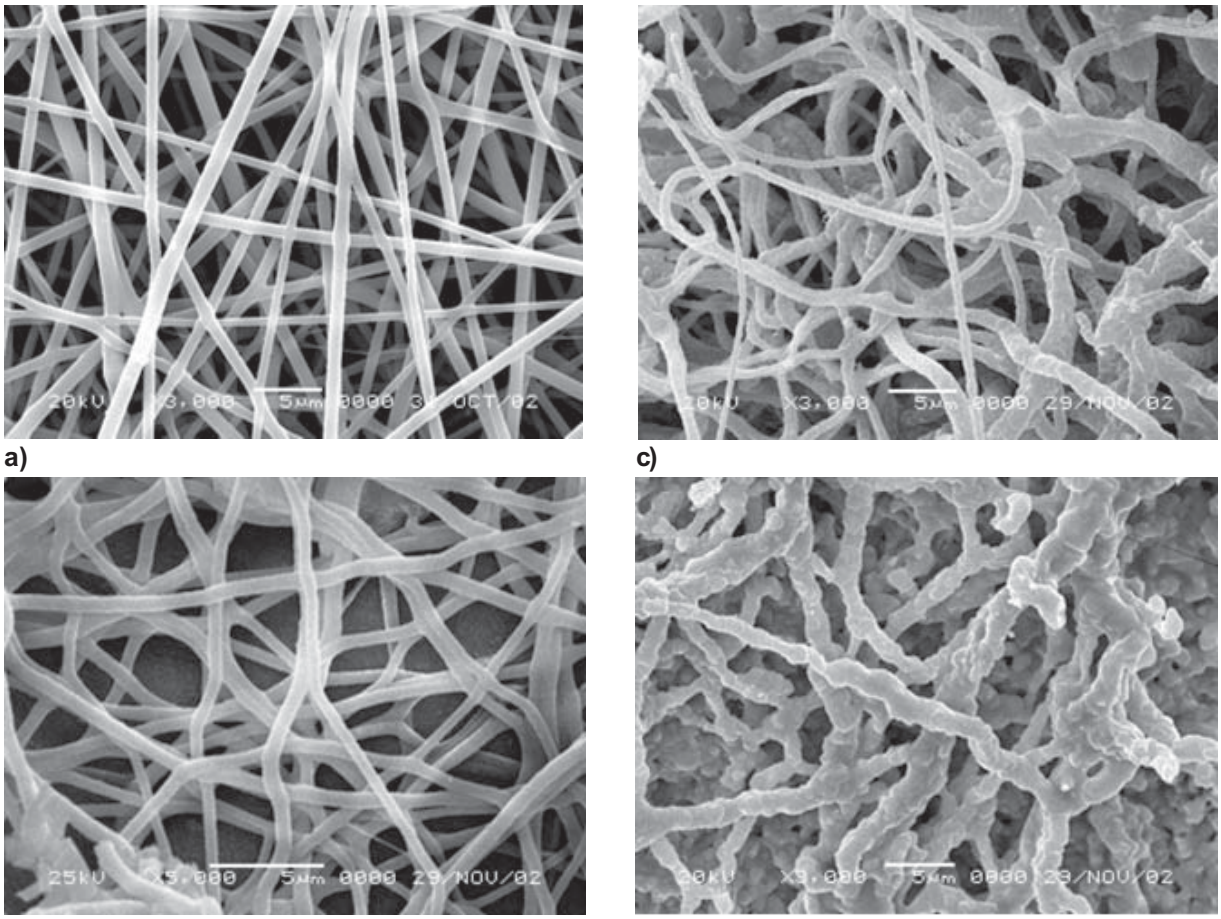

Fig. 1. SEM images of 50 wt% GeO_2 fibers a) as synthesized materials with PVAC composite; b) calcined at 500 °C; c) calcined at 700 °C and d) calcined at 1000 °C.

acetate) (PVAC) in acetone (14 wt%) as template. $Ge(OPr^i)_4$ starting material is dissolved in desired amount of isopropanol. A few drops of propionic acid are added to the above solution. The addition of propionic acid is used to reduce the hydrolysis rate of $Ge(OPr^i)_4$. Deionized water is added slowly to the solution, drop by drop until a molar ratio of H_2O : Ge = 1 :1. The solution is aged at room temperature in covered containers for 1-2 days, under continuous stirring. The electrospinning solution is prepared by dissolving the PVAC (14 wt%) solution with germanium oxide sol solution (3:1 wt ratio) under stirring for 5 h.

The electrospinning solution is taken in a syringe and delivered at a constant flow rate using a capillary. The positive (anode) terminal of a variable high voltage transformer capable of delivering 30 kV is attached to a copper wire inserted into the solution in the syringe and the negative terminal being attached to a aluminum foil covered collector (cathode). Upon applying a high voltage 15 kV into the solution with the distance between the capillary tip and the target surface being 17 cm, a fluid jet was ejected from the capillary. As the jet accelerated towards the cathode, the solvent evaporated and a charged fiber is deposited on the collector cathode. The deposited fibers are collected and subjected to heat treatment at different temperatures.

3. RESULTS AND DISCUSSION

The surface morphology of the electrospinning fibers have been studied by SEM. Usually the amount of metal content and temperature decides the morphological factors such as surface roughness, dendritic, spongy or powdery growth, *etc.* Fig. 1 shows the nature 50 wt% GeO_2/PVAC composite fiber. The

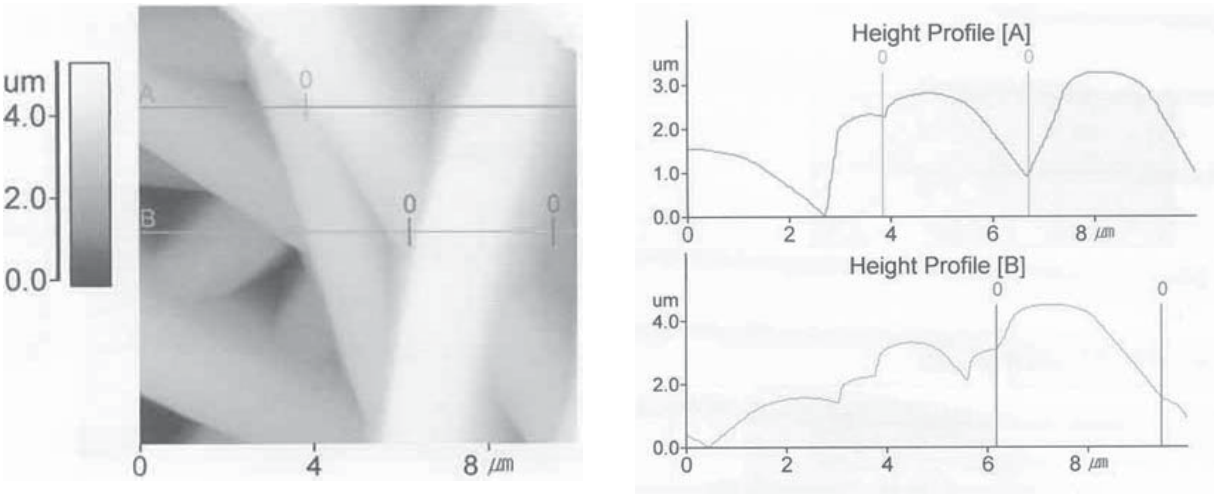

Fig. 2. AFM image of 50 wt% GeO_2 fibers with PVAC composite.

fibers have smooth surface, relatively straight and their diameters are rather uniform. The surface is changed and not appeared straight, when the fiber is given thermal treatment at 500 °C. During this temperature, the polymer decomposition begins. The surface of the fiber is changed into roughness at 700 °C due to the decomposition of all PVAC component. The fiber contains only GeO_2 component in this stage. Fig. 1c shows the fiber after calcination at 1000 °C, and it can clearly be seen that the cross section changes from circular to polygonal and that the roughness of the surface is obviously also increased.

In order to achieve a more direct insight into the surface structural feature of fibers, AFM technique has been employed. A two dimensional image of fibers with height profile are shown in Fig. 2, which clearly indicates the fiber structures. The strip at the right hand side part of figure indicates the Z-axis height from which it is possible to estimate the fiber roughness.

The powder X-ray diffraction (XRD) pattern as shown in Fig. 3 reveals the overall crystallinity and purity of the as-synthesized product. The XRD spectrum of PVAC/GeO_2 composite fibers shows that the fibers are in the amorphous form. When the fibers subjected to calcination at 300 °C and 500 °C, a broad peak appears. This indicates the crystallization begins in these temperatures. Upon increasing the calcination temperature to 700 °C, several peaks are observed due to the formation of crystalline GeO_2 fibers. The same diffraction pattern is observed at 1000 °C also. The positions of the XRD peaks show good agreement with those of the hexagonal GeO_2 (α-phase quartz like structure) listed in the standard handbook of XRD spectra.

4. CONCLUSIONS

The GeO_2 nanofibers have been synthesized by an electrospinning followed by heat treatment. The composite fibers have smooth surfaces and are

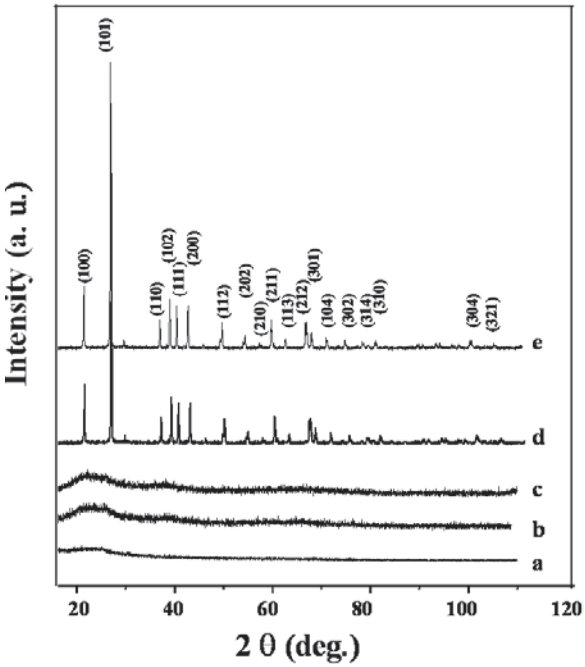

Fig. 3. X-ray diffraction patterns of 50 wt% GeO_2 fibers a) with PVAC composite, b) calcined at 300 °C, c) calcined at 500 °C, d) calcined at 700 °C, and e) calcined at 1000 °C.

straight in length. Analysis of the structures after heat treatment shows that, the PVAC component undergoes decomposition and the fibers attain hexagonal fibrous crystals.

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