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Effect of aluminum oxide doping on the structural, electrical, and optical properties of zinc oxide (AOZO) nanofibers synthesized by electrospinning

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ABSTRACT

Zinc oxide nanofibers doped with aluminum oxide were prepared by sol–gel processing and electrospinning techniques using polyvinylpyrrolidone (PVP), zinc acetate and aluminum acetate as precursors. The resulting nanofibers were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV–Vis spectroscopy, and current–voltage (*I–V*) properties. The nanofibers had diameters in the range of 60–150 nm. The incorporation of aluminum oxide resulted in a decrease in the crystallite sizes of the zinc oxide nanofibers. Aluminum oxide doped zinc oxide (AOZO) nanofibers exhibited lower bandgap energies compared to undoped zinc oxide nanofibers. However, as the aluminum content (Al/(Al + Zn) × 100%) was increased from 1.70 at.% to 3.20 at.% in the electrospinning solution, the bandgap energy increased resulting in lower conductivity. The electrical conductivity of the AOZO samples was found to depend on the amount of aluminum dopant in the matrix as reflected in the changes in oxidation state elucidated from XPS data. Electrospinning was found to be a productive, simple, and easy method for tuning the bandgap energy and conductivity of zinc oxide semiconducting nanofibers.

1. Introduction

Zinc oxide is a well-known wide-band gap wurtzite structured semiconducting oxide material which lies on the border between ionic and covalent semiconductors [1]. Pure and doped zinc oxide nanostructured materials have recently attracted considerable interest due to their unique physical properties and a wide range of possible applications [2–4]. However, pure zinc oxide is not stable in air and its electrical properties are significantly affected by adsorption of O_2, CO_2, hydrocarbons, S-containing compounds, and water [5]. Therefore, single crystals and polycrystalline films of zinc oxide have been doped to enhance their mechanical, electrical, and optical properties with elements of the alkali metals such as Li and with Ga, In, N, Al, Sn, and P from groups IIIB to VIIB [5].

Alumina doped zinc oxide is investigated in this work due to its wide applications in particle form as a transparent conducting oxide in the electric and optoelectronic industries [6]. Other dopants may also be used and will be investigated in future work. It has applications as a conducting window material for solar cells [7] as well as for active layers of light emitting diodes and laser diodes emitting in the UV spectral region [8]. It is also being investigated for applications in electrophotography [9], gas sensing [10], and thermoelectrics [11]. Undoped and doped zinc oxide films have been usually grown by various deposition techniques, such as pulsed laser deposition [12], DC magnetron sputtering [13], RF magnetron sputtering [14], metal organic chemical vapor deposition [15], molecular beam epitaxy [16], metal organic vapor phase epitaxy [17], reactive deposition [18], spray pyrolysis [19], sol–gel [20,21], and electrospinning [22,23] on different substrates.

Among these methods, electrospinning provides a simple, straightforward way to fabricate one-dimensional nanostructures. One-dimensional alumina doped zinc oxide nanostructures offer a very interesting class of materials for a wide variety of applications in different kinds of devices. A range of one-dimensional polymeric, composite, and ceramic materials have been successfully synthesized by this technique with the characteristic features of easy control of fiber morphology, low cost, and safety [24–28]. There are, however, only a few published reports available on the effect of dopant addition on morphological, electrical, and optical properties of semiconducting oxide nanofibers obtained by electrospinning.

In the present study, electrospinning was used to synthesize aluminum oxide doped zinc oxide (AOZO) nanofibers. Modifications of

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Table 1
Metallic elemental compositions and microstructural parameters of the four different aluminum oxide doped zinc oxide (AOZO) nanofiber samples after calcining at 873 K for 5 h.

Sample	Atomic ratio in electrospinning solution, Al/(Al + Zn) × 100%	Volume of the unit cell (Å)^3	Average crystallite size (nm)
ZnO (undoped)	0	47.58	41.78
AOZO1	1.7	47.26	32.16
AOZO2	2.4	47.28	36.35
AOZO3	3.2	47.38	38.01

the crystal structure, optical absorption properties, electrical conductivity and chemical makeup brought about by doping of these nanofibers have been studied. These AOZO nanofibers have potential applications in catalytic, photocatalytic, photonic, electronic, and sensor devices.

2. Experimental

AOZO nanofibers were prepared by adding sol–gel precursors to polymer solution and by electrospinning the polymer solution. Details about the electrospinning of nanofibers can be found elsewhere [24–28]. For the zinc oxide precursor solutions, zinc acetate ($Zn(CH_3COO)_2$) was dissolved in water at a mass ratio of 1:4 of $Zn(CH_3COO)_2$ to water. A polyvinylpyrrolidone (PVP)–ethanol solution of a mass ratio of 1:6 of PVP to ethanol was added to the aqueous zinc acetate solution at a mass ratio of 1:1.5. The aluminum oxide precursor solution prepared with a mass ratio of 1:1:1 of aluminum acetate ($Al(CH_3COO)_3$) to water to ethanol was magnetically stirred for 24 h at room temperature. Another PVP solution, mass ratio of 3:40 of PVP to ethanol, was added to the aluminum acetate solution at a mass ratio of 1.7:1 of PVP to aluminum acetate. The amount of this PVP/$Al(CH_3COO)_3$ composite solution that was added to the PVP/$Zn(CH_3COO)_2$ solution was varied to form the electrospinning solution according to the amount of doping desired. The electrospinning solution was magnetically stirred for 1 h at room temperature before electrospinning.

The electrospinning solutions were electrospun at a voltage of 20 kV and constant solution flow rate of 5 μl/min with a 20 cm distance from the needle tip to the fiber collector. The electrospun fibers were collected on the surface of a grounded aluminum foil. These as-spun fibers were heated to 873 K at the rate of 10 K/min and then kept at 873 K for 5 h to yield ceramic nanofibers. Compositions and characteristics of four different AOZO samples used in this investigation are summarized in Table 1.

The electrical conductance of the solution was measured with an Omega conductometer (model: PHH-80BMS) while the viscosity was measured with a viscometer (Brookfield dial viscometer, Brookfield engineering laboratories, Inc., USA) at room temperature. The average fiber diameter and morphology of different samples were measured by scanning electron microscopy (SEM) analysis. Grain sizes and other microstructural parameters of four different AOZO nanofiber samples were measured with X-ray diffraction (XRD) analysis. Absorption edges and hence optical bandgap energies of the nanofiber samples were measured using UV–Vis spectroscopy in diffuse reflectance mode. The ceramic fibers were brittle and it was difficult to attach the electrical contacts onto the fiber mat or to attach fiber mat to a solid substrate. Therefore, for electrical property measurement, the AOZO nanofibers were ground into powder and pressed into disks (6 mm diameter and 0.75 mm thick) and electrical contacts were made onto two flat surfaces of the disks. For all other characterizations, nanofiber mats as obtained after heat treatment were used without any further sample preparation.

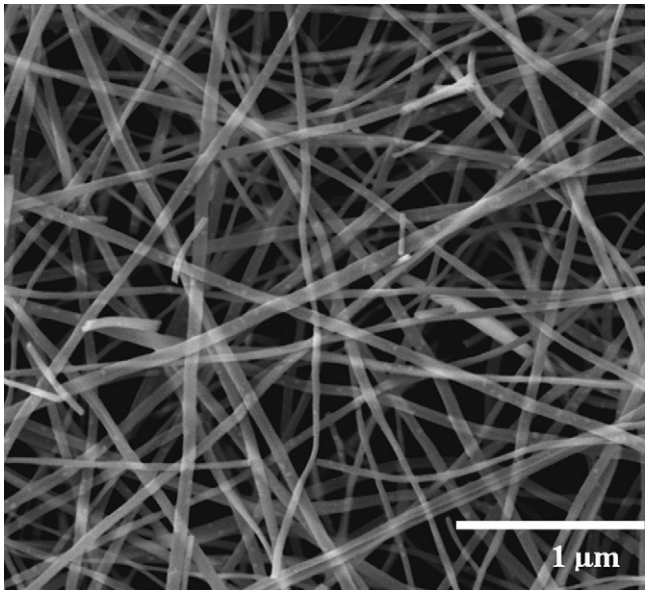

Fig. 1. Representative SEM image of aluminum oxide doped zinc oxide nanofibers (sample AOZO1) exhibiting an average fiber diameter 100 nm after being calcined at 873 K for 5 h.

3. Results and discussion

3.1. Scanning electron microscopy (SEM)

For SEM (Hitachi S-2150) analysis, the nanofibers were placed on an aluminum stub with a strip of carbon tape applied to the surface to promote fiber adhesion while minimizing charging effects. The samples were silver-coated (S150B Sputter Coater, Edwards), and imaged using an accelerating voltage of 20 kV. Average fiber diameters were calculated from 50 data points. Fig. 1 shows a representative SEM image of AOZO1 nanofibers. The range of diameters for AOZO nanofibers was determined to be 60–150 nm. The average diameters of the AOZO nanofibers were found to decrease with the increase of aluminum (Al^{3+}) content in the precursor solution. This can be attributed due to the fact that increasing the Al^{3+} content

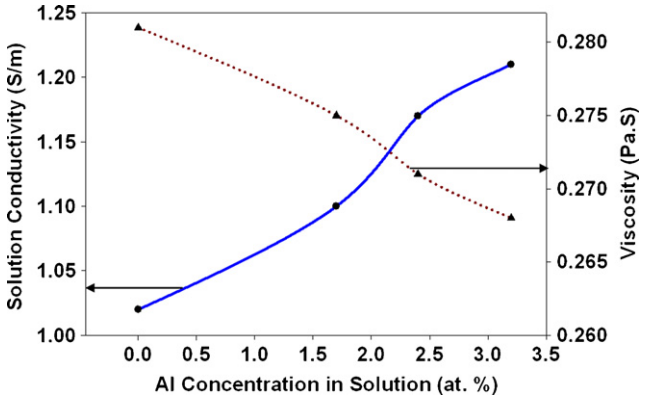

Fig. 2. Conductivity and viscosity of electrospinning solutions at different concentration of Al-dopant.