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Review

Uniaxially aligned ceramic nanofibers obtained by chemical mechanical processing

R. Tararam [a], C.R. Foschini [b], F.B. Destro [c], A.Z. Simões [c,*], E. Longo [a], J.A. Varela [a]

[a] Univ Estadual Paulista – UNESP – Instituto de Química, Rua Prof. Francisco Degni n° 55, CEP 14800-900 Araraquara, SP, Brazil
[b] Univ Estadual Paulista – UNESP – Faculdade de Engenharia de Bauru, Dept. de Eng. Mecanica, Av. Eng. Luiz Edmundo C. Coube 14-01, CEP 17033-360 Bauru, SP, Brazil
[c] Univ Estadual Paulista – UNESP – Faculdade de Engenharia de Guaratinguetá, Guaratinguetá 12516-410, SP, Brazil

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ABSTRACT

For this study, we investigated a simple method to generate well aligned nanofibers over large areas using an organic polymer stretched over the substrate surface With this method, ZnO and CuO 3D parallel nanowire arrays were successfully prepared by calcinations of the polymer fibers. X-ray diffraction (XRD) analysis revealed that the copper oxide has a monoclinic structure while the zinc oxide has a hexagonal structure. Scanning electron microscopy (SEM) analysis showed ceramic nanofibers with an average diameter of 120 nm which were composed of small nanoparticles which are 10 nm in diameter. The ability to obtain uniaxially aligned nanofibers reveals a range of interesting properties with potential applications for sensors, catalysts and energy technologies.

Contents

1. Introduction

Several advantages of using nanofibers and nanowires are reported in the literature. Due to their high aspect ratio, the control of surface chemical interactions is critical for sensors and catalysts. Although few authors have successfully obtained the deposition of oriented fibers, randomly distributed nanofibers can easily be obtained by electrospinning; e.g., ZnO [1–3] and CuO [4–6] Dabirian et al. [7] employed centrifugal forces during electrospinning to align fibers while Li et al. [8] reported the application of electric fields in electrodes during the deposition by electrospinning to achieve fiber orientation. In both cases, problems with low deposition rates in small surface areas created difficulties for practical applications. Today, gas sensors are available in the market for automotive and health applications as well as more traditional areas such as alarms sensitive to toxic or explosive gases. To develop better, cheaper, faster, more sensitive and selective sensors, new research is focused on nanostructured sensors [9,10]. There is a demand for new functional materials, different ways of preparation and contact configurations. Researchers are investigating new active gas sensors with appropriate characteristics for their specific functionalities [11–15].

With recent progress in the nanoscience field, micro- and nanosensors of metallic oxide are produced; e.g., the production and manipulation of metallic oxide nanowires. However, manipulating

* Corresponding author.
E-mail address: alezipo@yahoo.com (A.Z. Simões).

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individual nanowires to apply them to large-scale production poses a huge problem. Due to their small dimensions, micro- and nano-sensors can be heated locally which facilitates energy savings as well as better integration of different materials, when larger selectivity is desired [16,17].

These quasi-one-dimensional Q1D structures have a high aspect ratio (surface area per volume) and demonstrate a superior sensitivity to chemical surface processes. In addition, Q1D structures not only have characteristics of the macroscopic crystal such as piezoelectricity, chemical sensibility and photodetection, but also introduce new properties associated with the confinement of their dimensions and their high geometric anisotropy [18,19]. Several previous studies illustrate that nanowires show potential applications as gas sensors, chemical and biological sensors, micro lasers and displays. Nanowires based on super-lattices and p–n junctions in a single nanowire have previously been researched. The development of nano-field effect transistors (FETs), light emitting diodes (LEDs), bipolar junction transistors and logical circuits is quite promising with potential applications for metallic oxide nanowires in the nano-device area [20].

Charifi et al. [21] employed ab initio techniques to investigate structural, electronic and optical properties of ZnO compounds; they reported that 3d orbitals of the Zn atom were treated as the valence band (VB) with an indirect band gap of 1.47 eV. Bouderbala et al. [22] synthesized undoped ZnO thin films of different thicknesses by radio frequency (r.f.) sputtering to study the effect of thickness on their structural, morphological, electrical and optical properties. These authors noted an increase in the grain size versus the thickness while electrical properties measurements revealed behavior which is very dependent upon thickness. Optical measurements confirmed that all samples have a strong transmission which is higher than 80% in the visible range. A slight shift in the absorption edge towards large wavelengths was observed as the thickness increased; this result confirms that the band gap decreases slightly from 3.37 to 3.32 eV, and the film thickness varies from 0.32 to 0.88 mm. In other research, Reshak et al. [23] obtained inorganic ZnO nano-crystallite (NC) which was incorporated into photopolymer matrices (7.5% by weight) and optically treated by coherent bicolor nano-second laser pulses with Er^{3+} glass laser lines at 1.54 and 0.77 μm. Sufficiently good effective second-order susceptibility coefficients (up to 2.8 pm/V) at wavelengths of 1.54 μm were achieved. The maximum second-order optical susceptibility was achieved for NC sizes equal to about 30 nm. Ozga et al. [24] studied photoinduced second harmonic generation (SHG) in Au nanoparticle-deposited ZnO (NC) films which they explored by applying a bicolor coherent treatment of a Nd-YAG laser with a wavelength of 1.06 μm and its SHG. These authors have established that the co-existence of ZnO and Au nanoparticles produces a substantially larger SHG output with respect to pure ZnO NC deposited on the glass substrate which reaches a second order susceptibility of about 23 pm V^{-1}. Better nonlinear optical susceptibilities were obtained during photo treatment at temperatures near 30–35 °C for Au doped samples; Samples without gold NCs are temperature-independent, and generally, an increasing in the temperature produces a decrease in the optical SHG. CuO nanowires were prepared on copper foil by thermal oxidation in air. The effect of annealing temperature and growth time on the nanowire morphology was investigated which revealed that the annealing temperature and the growth time are important in the CuO nanowire morphology such as the density, *t* length and diameter. The length and density of nanowires increase with prolonging growth time [25]. Du et al. [26] prepared porous ZnO photocatalysts by a facile method; i.e., the thermal treatment of zeolitic imidazolate framework-8. The calcination temperature and time significantly influenced the ZnO morphology, composition and pore structure. Photocatalytic activities of as-prepared ZnO powders were evaluated in the degradation of methylene blue (MB) under a UV light in comparison with commercial anatase TiO_2 and Degussa P25 TiO_2. The surface area and crystallinity of porous ZnO obviously affected the photocatalytic activity of ZnO. The ZnO prepared at 500 °C for 5 h (ZnO-500-5) exhibited the highest photocatalytic activity which was higher than the photocatalytic activity of the commercial anatase TiO_2 and lower than the photocatalytic activity of Degussa P25 TiO_2.

ZnO nanofibers doped with different Al concentrations were fabricated by the electrospinning method; these nanofibers have a hexagonal structure with a diameter of about 150 nm. The nanofiber grain size decreases after La doping. PL spectra of all samples have two luminescence bands at green and orange centers. These bands can be attributed to oxygen vacancies and an excess of oxygen [27]. Zhao et al. [28] reported the fabrication of Mg doping on the crystal structure, morphology and optical properties of ZnO nanofibers obtained by the electrospinning method whereas the surface area-to-volume ratio is one or two orders of magnitude more than the ratio of continuous thin films. For this study, we investigated a simple and versatile method to develop ceramic nanofibers based on ZnO and CuO uniaxially aligned over large areas. One-dimensional structures were obtained as a result of both mechanical processing and the thermal treatment of organic fibers containing metallic precursors.

2. Experimental procedures

The novel approach to the spinning process described in this work differs from the well known electrospinning technique which was already studied earlier [29–31]. The typical electrospinning method consists of extruding a polymeric fluid from a needle in an electric field which was successfully exploited to generate thin fibers from a broad range of polymers. However, electrospun fibers are often collected as randomly oriented structures with slow deposition rates on small surface areas. This study establishes a new method which involves a combination of chemical and mechanical forces to a spinning process over larger surface areas and higher deposition rates. A special polymer which can be highly stretched between two moving plates to form filaments in the air gap was employed. An alternative configuration using two rolls spinning in contact facilitates continuous production of polymer ultrathin fibers which is related to a method for simultaneously spin stretching the polymer in the spinning device.

Fig. 1 displays the process flowchart of technical operations and illustrates the apparatus employed for fiber production. The initial step involves the preparation of the composite fluid which is formed from the polymer solution mixed with a metal salt solution (e.g., Cu^{2+} and Zn^{2+} ions). Then a drop of the composite fluid is dispersed on the roll surface (coating roll) to evaporate the solvent. This viscous polymeric coating can be stretched out mechanically by using the device shown in Fig. 1b which is composed of two cylinders rotating in contact (in opposite directions). Multifilaments of the fibers are formed in the air gap between the junction point of the cylinders and the substrate. A close inspection reveals that the fibers are always parallel and well aligned due to the extensional flow in the moving surface of the cylinders. The fibers are collected by correct positioning of the substrate, but there is still the possibility of using jets of compressed air to expel the fibers to obtain a random distribution which is similar to the electrospinning technique but with much larger deposition rates. The last step is the calcination of composite fibers above 500 °C to eliminate the organic material; only the desired metallic oxide remains in the form of wires. The process can also be used with more than one metallic cation in the stoichiometric composition so complex ceramic nanofibers can be obtained which results in promising perspectives (e.g., gas sensors: $CaCu_3Ti_4O_{12}$ [32], $NiFe_2O_4$ [33], $SrTiO_3$ [34]).

The complete process of fiber production (the spin-stretching technique) is limited by viscoelastic properties of the composite fluid. The stretchability of the composite can be altered depending of the metal solution added and the solvent used; i.e., stretching of at least 1 m without breaking the filament. Therefore, larger rolls could cover an area of 1 m^2 with fibers uniaxially aligned, and currently no technique exists whereby ceramic nanowires with these dimensions can be achieved,

Samples were characterized by field-emission scanning electron microscopy (FEG-SEM) (JEOL, Model 7500F) and energy dispersive spectroscopy (EDS) microanalysis. The phase characterization of these ceramic nanofibers was evaluated by XRD using Cu Kα radiation (diffractometer Model RIGAKU DMAX/2500 PC with a rotary anode operating at 150 mA and 40 kV). The crystallite size (d) of the metal oxide was calculated using Scherrer equation $d = k\lambda/\beta \cos\theta$, where k is constant, λ is wavelength of X-rays and β is the full width at half maximum (FWHM) reflections measured from slow scan, where θ is the diffraction angle of the main peak. TG