Sensors and Actuators B 145 (2010) 592–595

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Short communication

SnO_2–ZnO hybrid nanofibers-based highly sensitive nitrogen dioxides sensor

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ARTICLE INFO

Article history:
Received 24 August 2009
Received in revised form 2 November 2009
Accepted 11 November 2009
Available online 17 November 2009

Keywords:
Nanofiber
Electrospinning
Pulsed laser deposition
ZnO
SnO_2
Gas sensing

ABSTRACT

SnO_2–ZnO hybrid nanofibers were fabricated by combining the electrospinning and the pulsed laser deposition methods. After calcining at 600 °C, the nanocrystalline SnO_2 coated ZnO nanofibers with a random network structure were obtained. The fiber diameter and the size of SnO_2 deposit were 55–80 nm and 10–15 nm, respectively. SnO_2–ZnO hybrid nanofibers-based sensor exhibited very high gas response to NO_2 concentration as low as 400 ppb level at 200 °C.

1. Introduction

Semiconducting metal oxides (SMOs) with nanostructures as gas sensing materials have been widely used in detection of toxic gases and vapors [1–3]. Typically, the gas sensing properties of the SMO-based sensors are highly dependent not only on their surface chemical reactivity and thermal stability, but also on the geometrical and compositional variations [4–7]. Recently, SMOs with one-dimensional (1D) nanostructures such as nanowires, nanorods, and nanofibers have been a subject of intensive research in gas sensing area because of their unique properties and interesting applications [8–10]. Many researches focus on the nanofibers which provide large surface-to-volume and length-to-diameter ratios, which contribute to the high sensitivity. Some techniques such as metal-organic chemical vapor deposition (MOCVD) [11], chemical vapor deposition (CVD) [12], carbothermal reduction synthesis [13], vapor–liquid–solid (VLS) [5], electrospinning (ES) [14] have been attempted to obtain 1D nanostructured SMOs. Some techniques have been attempted to obtain 1D nanostructured SMOs. In particular, the electrospinning (ES) method is a very attractive method for the fabrication of nanofibers, considering simplicity, reproducibility, flexibility and manipulation.

Among available SMOs, the ZnO is one of the most well-defined gas sensing materials. The fabrication and characteristics of electrospun ZnO nanofibers has been reported [15–17]. However, the gas sensing properties of the ZnO nanofibers upon exposure to oxidizing and/or reducing gases of low concentration level still remain poor. It is worth mentioning at this point that the ZnO nanofibers can be further functionalized by surface modification with various catalysts, nanoparticles, and biological species, leading to achievement of exceptional gas response.

In this study, we report on the fabrication of ZnO nanofibers using an ES method and the response of ZnO nanofibers upon NO_2 gas that is the major cause of air pollution and acid rain. In order to improve the gas response of ZnO nanofibers to low NO_2 concentration, we have coated a thin layer of nanocrystalline SnO_2 on the ZnO nanofibers. SnO_2 is an n-type SMO gas sensing material with excellent gas response toward exposure of environmental gases. SnO_2 was deposited using a pulsed laser deposition (PLD) method. The NO_2 sensing properties as well as the structure of SnO_2 coated ZnO (SnO_2–ZnO) nanofibers were investigated.

2. Experimental

To prepare the ES solution, 5 g of Zn acetate dihydrate ($Zn(CH_3COO)\cdot 2H_2O$, Inostek) with 0.8 mol was mixed with 3 g of PVP (poly(4-vinyl phenol), Aldrich, M_w = 20,000) and then stirred for 3 h at 60 °C. Thereafter, 1 ml of ethanol was added to the mixture and then was sufficiently stirred to obtain a homogeneous solution. Finally, an ES solution with an optimized viscosity suitable for ES was obtained. To perform the ES process, the ES solution was loaded into a plastic syringe equipped with a needle. A needle of 250 μm in diameter was connected to a high voltage power supply. The feeding rate was kept constant at 0.3 ml/h using a syringe

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doi:10.1016/j.snb.2009.11.023

pump. The SiO_2/Si substrate was placed 5 cm below the needle tip to collect the electrospun composite fibers. The applied voltage was maintained at 7 kV. The substrate temperature was maintained at 80 °C during the ES process. The collecting time was about 5 min. In order to measure the gas sensing properties of the resultant nanofibers, the electrospun composite fibers were collected on platinum interdigital electrodes (Pt-IDEs) patterned SiO_2/Si substrate. The finger width, the finger gap and the overlap length of Pt-IDE were 15 μm, 10 μm and 500 μm, respectively. The electrospun composite fibers were hot-pressed at 120 °C to densify the non-woven mat of composite fibers. Subsequently, the composite fibers were baked on a hotplate at 250 °C for 30 min to remove the solvent. Thereafter, the ZnO/PVP composite fibers were calcined at 600 °C for 1 h in air to decompose the PVP and crystallize the ZnO. The SnO_2 deposit was coated on the ZnO nanofibers using a PLD method with KrF excimer laser (λ = 248 nm). The oxygen pressure, laser intensity and repetition rate were 26.66 Pa, 3 J/cm^2 and 2 Hz, respectively. PLD process was carried out at room temperature for 1 min. Finally, to crystallize SnO_2 deposit, the SnO_2 coated ZnO nanofibers were annealed at 600 °C for 30 m in air. In order to measure the gas sensing properties of the resultant nanofibers, the ZnO and SnO_2–ZnO nanofibers were collected on Pt-IDEs patterned SiO_2/Si substrates. The IDEs have dimensions of finger width of 15 μm, the finger gap of 10 μm and the overlap length of 500 μm, respectively.

For NO_2 gas sensing test, the SnO_2–ZnO hybrid nanofibers-based sensor was placed in a sealed chamber equipped with heater and gas supplying units. The applied voltage was fixed at 100 mV. Various NO_2 concentrations were obtained by diluting a premixed gas of NO_2 20 ppm with dry air. The NO_2 response was determined by comparing the resistance of SnO_2–ZnO hybrid nanofibers in dry air (R_{air}) to that in NO_2 (R_{NO_2}). The response is defined as R_{NO_2}/R_{air}.

3. Results and discussion

Fig. 1 shows the scanning electron microscopy (SEM) images of the electrospun ZnO/PVP composite fibers, the pristine ZnO nanofibers, and the SnO_2–ZnO hybrid nanofibers. The assembly of the ZnO/PVP composite fibers forms a multi-layered random network structure which is due to the instability of the spin jet, as shown in Fig. 1(a). The diameters of fibers were in a range of 250–350 nm. The surface morphology of the composite fibers appears to be smooth due to the polymeric feature. Fig. 1(b) shows the SEM images of pristine ZnO nanofibers obtained by calcining ZnO/PVP composite nanofibers. Although drastic shrinkage occurred after calcination, the ZnO nanofibers retained the network structure with the diameter of 55–80 nm. The pristine ZnO nanofibers have the one-dimensional nanostructures linked by the nanosized ZnO grains between 20 and 80 nm. Fig. 1(c) shows the SEM image of the SnO_2–ZnO hybrid nanofibers. Apparently, the ZnO nanofibers are covered with the SnO_2 nanoparticles of 10 –15 nm.

The bright-field scanning transmission electron microscope (STEM) images (Fig. 2(a)) indicates that a SnO_2–ZnO hybrid nanofiber of 72 nm in diameter in which polycrystalline SnO_2 and ZnO phases coexist. Fig. 2(b) shows elemental mapping images of Zn (red) and Sn (green) obtained using an electron dispersive spectroscopy (EDS) embedded in the STEM of ZnO nanofiber. This result reveals that the SnO_2 deposit (green) covers the ZnO nanofiber (red).

The XRD pattern of Fig. 3 shows that the SnO_2–ZnO hybrid nanofibers is in the polycrystalline structure with two phases of rutile SnO_2 (JCPDS 41-1445) and würtzite ZnO (JCPDS 36-1451) phases. This indicates that the annealing at 600 °C is sufficient to not only to decompose the PVP but also crystallize both ZnO and

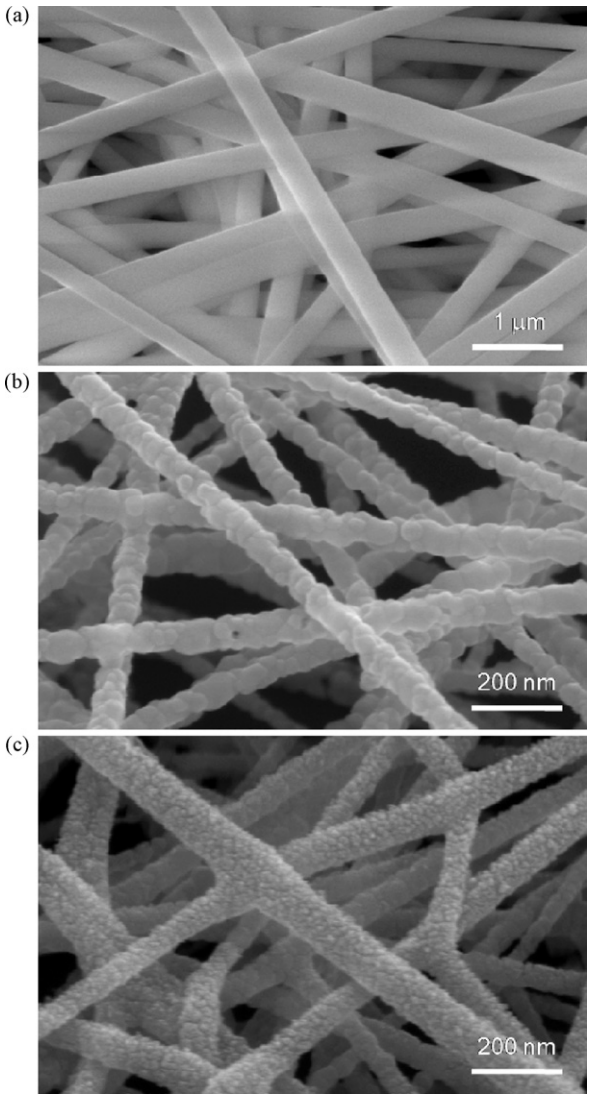

Fig. 1. SEM images of (a) the electrospun ZnO/PVP composite fibers, (b) the pristine ZnO nanofibers, and (c) the SnO_2–ZnO hybrid nanofibers.

SnO_2. No third phase such as Zn_2SnO_4 was observed. Due to the 1D geometry of nanocrystalline oxides and the enhanced functionalizing due to SnO_2, the SnO_2–ZnO hybrid nanofibers are expected to have enhanced gas sensing properties.

Fig. 4 shows that the responses of the SnO_2–ZnO hybrid nanofibers-based sensor are highly dependent on the working temperature (T_W) and the concentration of NO_2. The sensor exhibited relatively high response at the T_W between 180 °C and 200 °C at a fixed NO_2 concentration of 3.2 ppm (Fig. 4(a)). Thus, we choose 200 °C as our T_W in evaluating the SnO_2–ZnO hybrid nanofibers-based sensor. As the NO_2 concentration increases from 0.4 ppm to 4 ppm, the response at 200 °C increases from 6 to 105 as shown in Fig. 4(b). In contrast, the pristine ZnO nanofiber-based sensor showed poor response lower than 1.15. The increase in the resistance of the SnO_2–ZnO hybrid nanofibers upon exposure to NO_2 can be described by the following surface electrochemical reaction processes [14,18]:

$$NO_2(g) + e^- \leftrightarrow NO_2^-(ads) \quad (1)$$

$$NO_2(g) + e^- \leftrightarrow O^-(ads) + NO(g) \quad (2)$$

where "g" and "ads" refer to gas and adsorbate, respectively. Both reactions result in removal of free electrons (e^-s). The