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Nanowire structured SnO_x–SWNT composites: High performance sensor for NO_x detection

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ABSTRACT

A nanowire structured nanocomposite of tin oxide (SnO_x) and a single-walled carbon nanotube (SWNT) are fabricated using rheotaxial growth and thermal oxidation method for gas sensor application. The morphology, gas sensing properties, as well as the chemical and electrical properties are investigated. The oxidation temperature for Sn mainly determines the stoichiometry of the SnO_x nano-beads, and consequently the electrical and gas sensing properties of the nanocomposite sensors. The gas sensing to nitrogen oxide, hydrogen, oxygen, xylene, acetone, carbon monoxide, and ammonia are also examined to determine the gas selectivity of the sensor. The high sensitivity and selectivity towards NO_x of the nanocomposite sensor is realized via the porous structure of the SWNT template. The gas sensing mechanism of the nanocomposite structure is also discussed.

1. Introduction

Carbon nanotubes (CNTs) have recently been studied for their gas sensor applications because of their small size, high electrical conductivity, and good response even at low temperatures [1,2]. The authors also examined a porous mat structure of single-walled carbon nanotubes (SWNTs) for detection of NH_3 and NO_x (mixture of NO and NO_2) [3]. The SWNT-based gas sensors showed good responses to NH_3 and NO_x at room temperature, although the selectivity and the recovery behavior were poor. The recovery behavior could be improved by enhancing the operation temperature as in the metal oxide sensors.

Trials to form composites of carbon nanotubes with polymer, metal, and/or metal oxide were also carried out [4–6]. Thin films of multi-walled carbon nanotubes (MWNTs) and tin oxide composites have been reported to show high response to ethanol or ammonia at either room or moderate temperatures [7,8]. However, while the composites were fabricated by electron beam evaporation of a mixture of MWNTs and SnO_2 powders [7], or via spin-coating of a suspension of mixed MWNTs and SnO_2 nanoparticles [8], they revealed inherently compact thin films, thereby showing limited sensitivities. Another common route to synthesize composites of carbon nanotubes and metal oxide has been the wet chemical method [9,10]. It requires processing steps including synthesis of CNTs, collection, dispersion, functionalization, mixing with metal oxide solution, filtration, and oxidation, among many others. These processes often produce toxic agents, require long time reaction, and use expensive metal-alkoxide. Moreover, the materials synthesized as such need additional post-treatments for proper functioning. Unfortunately, the porous structure of the materials may be destroyed during the processing, leading to a degradation in the sensing performance [6,8].

Recently, we have developed a simple method to synthesize nanocomposites of tin oxide (SnO_x) and SWNTs for gas sensor application [11]. The key development processes were (i) the formation of porous thin film of SWNTs as a substrate and (ii) metal deposition on the substrate and oxidation. The metal oxide coating of the SWNT wires forms a nanowire composite structure. In this report, we examined the electrical and gas sensing properties of the SnO_x–SWNT nanocomposite materials. The effect of oxidation temperature on the electrical and gas sensing properties of the nanocomposites were also investigated. The response of the sensors with varying operation temperatures and variations in sensing mechanism were also discussed.

2. Experimental

The synthesis method for producing one-dimensional nanocomposites of SnO_x and SWNTs for gas sensors based on rheotaxial growth thermal oxidation (RGTO) method was described in [11]. In brief, the synthesis process includes: (i) the preparation of substrate with comb-type electrode pattern, (ii) *in situ* growth of SWNTs using the arc-discharge method, (iii)

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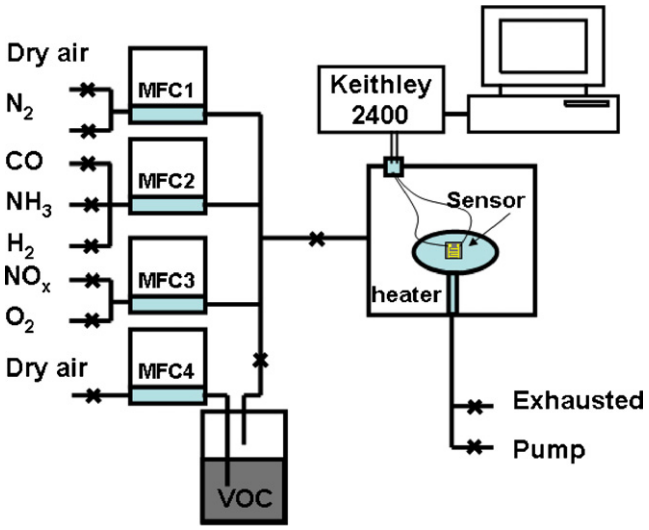

Fig. 1. The schematic diagram of sensing measurement system.

deposition of Sn on the SWNTs, and (iv) thermal oxidation of Sn. The oxidation was performed in air for 2 h with varying temperatures (T_{ox}) that ranged from 300 to 600 °C. The morphology of the synthesized nanocomposites was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The atomic composition was investigated by X-ray photoelectron spectroscopy (XPS).

The electrical and gas sensing properties of the synthesized sensors were tested using a home-made chamber system as schematically shown in Fig. 1 [3]. Gold wiring combined with silver paste was used for electrical contact with the sensor electrodes in the process of measuring the gas sensing properties. The sensors were placed on a hot chuck that can be controlled up to ~400 °C. The test gases used were 1000 ppm NO_x, 1000 ppm CO and 1000 ppm NH_3 with nitrogen balance, and concentrated H_2 and O_2. The concentrations of the test gases were controlled by four mass flow controllers (MFC1, MFC2, MFC3, and MFC4). Dry air was used for dilution. For the test with volatile organic compounds (VOCs) such as xylene and acetone, controlled evaporation of the liquid via bubbling was employed. The concentration of VOCs was calculated using equation [12]:

$$C\,(\mathrm{ppm}) = 10^6 \times \left(\frac{P_S}{P} \times \frac{f}{f+F}\right), \quad (1)$$

where f and F are the flow rates (in sccm) of the bubbling air saturated with VOC and the air as dilution gas, respectively; P is the total pressure; and P_S is the saturated vapor partial pressure obtained by Antoine equation [13]. The sensor response is defined by: $S(\%) = 100 \times (R_g - R_o)/R_o$ for oxidizing gas (NO_x, O_2), and $S(\%) = 100 \times (R_o - R_g)/R_g$ for reducing gas (H_2, CO, NH_3, and VOC), where R_o and R_g refer to the resistance in air and in the test gas, respectively.

3. Results and discussion

3.1. Morphology and properties of the nanocomposites

The sensor device images with patterned comb-type electrodes on the SiO_2 substrate are shown in Fig. 2(a). The substrate of 4 mm × 4 mm is composed of fingers and gaps with widths of 200 μm each. The morphology of the SnO_x–SWNTs nanocomposite is shown in Fig. 2(b), where nanowires of SWNTs coated with a tin oxide layer are apparent. Note that the SnO_x coating did not result in smooth tubes, but formed into beads along the nanotube bundle.

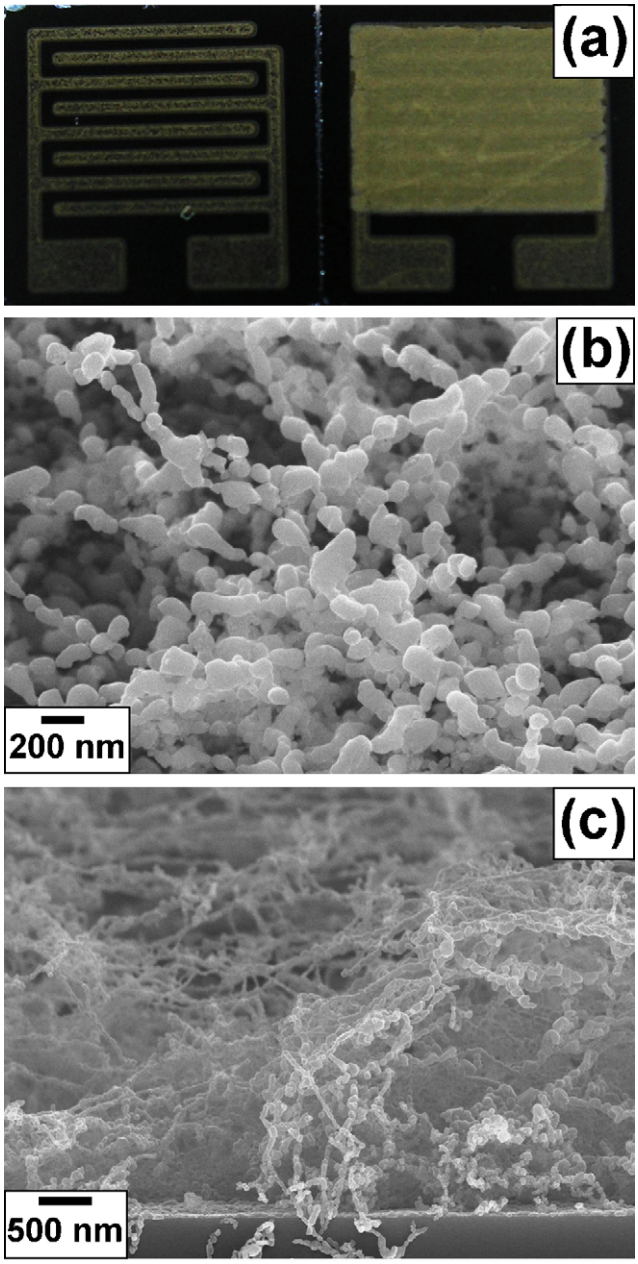

Fig. 2. Optical image (a) of patterned electrodes on SiO_2 substrate (left), after deposited sensing layer (right), surface (b) and cross-sectional (c) SEM images of nanocomposite oxidized at 400 °C for 2 h in air.

The details of the nanostructure were observed by high resolution transmission electron microscopy (HRTEM) as illustrated in Fig. 3. As can be seen, the tin oxide was deposited outside of the SWNT bundles. From the figure, we can also see that the general diameter of the bundles is ~4 nm, while that of the SnO_x nano-beads is ~20 nm. The appearance of the bead-shaped nanoparticulate of SnO_x is basically due to the high surface energy of Sn melt and its poor wetting on SWNTs. Thin-film-type SnO_x formed on the planar SiO_2 substrates also revealed an island-like morphology due to the poor wetting nature of tin [14,15]. This specific SnO_x morphology has been usefully implemented in producing porous thick film sensors.

The most important feature of the developed nanocomposite structure is its porosity. If an ensemble of nanostructures forms mat-type morphology on the substrates, the densely stacked nanostructures will have limited usefulness as gas sensors. This