Materials Science in Semiconductor Processing 26 (2014) 18–24

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Preparation and ethanol sensing properties of flower-like cupric oxide hierarchical nanorods

Nguyen Hoang Hung, Nguyen Dang Thanh, Nguyen Huu Lam, Nguyen Dac Dien, Nguyen Duc Chien *, Dang Duc Vuong *

School of Engineering Physics, Hanoi University of Science and Technology, Vietnam, 1 Dai Co Viet road, Hanoi, Viet Nam.

ARTICLE INFO

Available online 19 April 2014

Keywords:
Hydrothermal
Gas sensor
Flower-like CuO
PEG

ABSTRACT

Flower-like cupric oxide (CuO) hierarchical nanorods (petal size: 60–100 nm in diameter and 500–700 nm in length) were synthesized by wet chemical-assisted hydrothermal processing. The samples were characterized by field emission scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. The influence of hydrothermal temperature on the formation of CuO nanoflowers was investigated. Sensors based on CuO nanoflowers were fabricated by coating them on SiO_2/Si substrate attached with Pt interdigitated electrodes. Sensing characteristics of the samples were measured and evaluated as a function of operating temperature and ethanol vapor concentration. The results revealed that the p-type semiconductor CuO nanoflowers based sensors exhibit high sensitivity and selectivity toward ethanol vapor with the optimum working temperature at about 230 °C.

1. Introduction

Developed in parallel with nanotechnology, gas sensors play important roles in many fields such as industrial production, mining and traffic safety [1,2]. In recent years, much attention has been paid to the fabrication of gas sensors based on semiconducting metal oxides for the detection of hazardous, flammable and toxic gases, due to their rich sources, low cost, and ease of fabrication. Nanostructured gas sensing materials have been intensively studied due to their size and shape-induced chemical and physical properties. Up to now, n-type metal oxides have been widely investigated, such as SnO_2 [3,4], ZnO [5], α-Fe_2O_3 [6], and TiO_2 [7]. Recently, increasing interest has been taken in gas sensors based on p-type semiconductors, like CuO [8–10]. There have been reports on CuO nanowires [11], CuO nanosheets [12], CuO nanoribbons [13], hollow and hierarchical CuO micro-spheres [14,15], and CuO nanoparticles [16] used to detect various target gases (NO_2, H_2S, C_2H_5OH, HCHO, CO, and NH_3) in the working temperature ranging from 200 °C to 400 °C. However, CuO nanoflowers based gas sensors have seldom been reported on, and their sensing mechanism remains unclear.

The preparation of CuO nanostructures has been accomplished through several techniques [17]. Various morphologies of CuO were obtained by using a hydrothermal treatment method. Yang and He [18] used Cu $(NO_3)_2 \cdot 3H_2O$ as a starting material and polyethylene glycol (PEG) as a surfactant to prepare flower-like CuO materials with petals in the form of nanosheets. By using the hydrothermal micro wave method with PEG as a surfactant, Keyson et al. [19] successfully prepared CuO urchin-like microstructures. Yunling et al. [20] reported fabrication via the hydrothermal process of flower-like

* Corresponding author. Tel: +84 4 38693350; fax: + 84 4 38693498.
E-mail addresses: chien.nguyenduc@hust.edu.vn (N.D. Chien), vuong.dangduc@hust.edu.vn (D.D. Vuong).

http://dx.doi.org/10.1016/j.mssp.2014.03.052
1369-8001/

CuO nanomaterials (each flower petal is a nanosheet) with the assistance of cetyltrimethylammonium bromide (CTAB). Yang et al. [21] also reported a microwave-assisted hydrothermal (MH) process to prepare CuO nanorods. To our knowledge, flower-like CuO nanorods (NRs) derived from hydrothermal treatment using $Cu(NO_3)_2 \cdot 3H_2O$ as a starting material and PEG as a surfactant have not been reported yet.

In this work we report a simple, one-step synthesis of flower-like CuO nanostructures with each flower petal being a nanorod by using the hydrothermal treatment method with PEG as a surfactant. The dependence of CuO morphologies on hydrothermal temperature was studied and the formation mechanism of flower-like CuO hierarchical nanorods was proposed. Finally, ethanol vapor sensing properties of flower-like CuO were investigated.

2. Experimental

Cupric nitrate (99.5%, Fenxichun Chemical Co.) and ammonium bicarbonate were used as starting materials. PEG 4000 (Purchased from Merck) was used as structure directing templates. In brief, for typical synthesis, a starting solution of copper (0.45 mol L^{-1}) was prepared by dissolving 3.159 g (13 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ in 25 mL deionized water. Subsequently, the $Cu(NO_3)_2$ solution was slowly poured into 30 mL of NH_4HCO_3 solution (2 mol L^{-1}) under vigorous stirring, and a blue-colored precursor was obtained. The precipitate was collected and washed with deionized water several times and stirred for 1.5 h and then dispersed into 80 ml PEG solution 0.5 wt% under continuous stirring for 30 min at 60 °C to ensure complete dissolution of PEG. The mixed solution, after complete reaction, was sealed into a Teflon-lined stainless steel autoclave of 30 mL capacity and heated at 170 °C for 24 h. After that, the autoclave was cooled down to room temperature naturally. The black precipitate was washed with deionized water and absolute ethanol several times and finally dried at 100 °C for 6 h in air. The obtained product was heated to 600 °C at a rate of 1 °C/min and then maintained at 600 °C for 2 h in air. The detailed process of fabrication is shown in Fig. 1. The obtained materials were coated onto Pt-interdigitated electrodes with the gap between the fingers of about 30 μm by the spin-coating method and then dried in air at 80 °C for 24 h. The sensor sample was annealed at 600 °C for 2 h to evaporate organic species and to stabilize the materials structure.

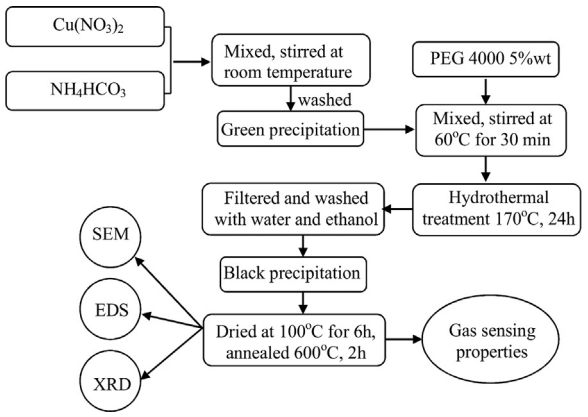

Fig. 1. Schematic diagram of experimental procedure.

A field emission scanning electron microscope (FE-SEM) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) attachment (HITACHI S4800) was used to perform morphological analysis and elemental composition analysis. The crystal structure of the samples was measured using an X-ray diffractometer (PANalytical-Philips X'pert Pro with CuKα radiation $\lambda = 1.54056$ Å).

The electrical resistance of the samples at different temperatures was measured as a function of the gas concentration. The sensors were placed in a glass test chamber and heated by an external source through the sample holder. The operating temperature of the sensors was determined with a thermocouple attached near the sensor element and varied in a wide range. The response of the sample to ethanol gas was thus measured in a static system. Herein, the sensor response was defined as the ratio R_{gas}/R_{air}, where R_{air} is the sample resistance in air and R_{gas} is its resistance in the presence of ethanol vapor.

3. Results and discussion

Fig. 2 shows FE-SEM images of the flower-like CuO material obtained through hydrothermal treatment at 170 °C for 24 h and calcined at 600 °C for 2 h. It can be seen from Fig. 2a and b, that the obtained nanoflowers consist of many CuO NRs. Highly uniform nano-sized flowers are obtained all over the sample. A high magnification FE-SEM image of the product (Fig. 2c) demonstrates a typical flower with rod size of 60–100 nm in diameter and several hundred nanometers in length.

Fig. 3a shows the X-ray diffraction (XRD) pattern of CuO powder after calcination at 600 °C for 2 h. All XRD peaks were assigned to monoclinic CuO (Pattern no. 01-089-5895) for all the samples with lattice constants of $a = 4.682$ Å; $b = 3.424$ Å; $c = 5.127$ Å and angles $\alpha = 90.00°$; $\beta = 94.420°$; $\gamma = 90.00°$. EDS analysis was performed to examine the composition and the result is shown in Fig. 3b. The peaks related to Cu and O emerged in the spectrum, and the atomic content of Cu/O was 46.38/53.62, close to 1:1. This result is consistent with some published papers [20,23].

The growth mechanism of flower-like CuO nanostructures can be described as follows. Firstly, $CuCO_3$ precipitate is formed by the chemical reactions

$$2Cu(NO_3)_2 + 2NH_4HCO_3 \rightarrow 2CuCO_3 + 5NO + NO_2 + 5H_2O \quad (1)$$

In hydrothermal condition, $CuCO_3$ is transformed into CuO by the following reaction:

$$CuCO_3 \rightarrow CuO + CO_2 \quad (2)$$

The formation of flower-like CuO nanostructures possibly follows the mechanism proposed in [22] which is illustrated in Fig. 4. According to this mechanism, PEG acts as a soft template for the formation of CuO flower nanostructures. In the initial stage, the aqueous solution