Sensors and Actuators B 186 (2013) 172–179

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Rhombus-shaped Co_3O_4 nanorod arrays for high-performance gas sensor

Zhen Wen, Liping Zhu*, Weimin Mei, Liang Hu, Yaguang Li, Luwei Sun, Hui Cai, Zhizhen Ye

State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Cyrus Tang Center for Sensor Materials and Applications, Zhejiang University, Hangzhou, 310027, PR China

ARTICLE INFO

Article history:
Received 27 February 2013
Received in revised form 26 April 2013
Accepted 27 May 2013
Available online 6 June 2013

Keywords:
Gas sensor
Facile synthesis
Rhombic Co_3O_4
Nanorod arrays
Ethanol sensing

ABSTRACT

Rhombic Co_3O_4 nanorod (NR) array-based gas sensor was successfully fabricated via a facile two-step synthesis approach, including the formation of rhombic Co(OH)F NR arrays as precursor followed by thermal conversion to porous Co_3O_4 without altering the original shape. Good ohmic contacts with the electrodes and intensive contact with the substrates avoided complicated fabrication process of gas sensors. The NR arrays annealed at 450 °C showed high-performance of ethanol detection. The response to 500 ppm ethanol gas reached ~71 and the optimal working temperature was as low as 160 °C. Meanwhile, the sensor exhibited good response/recovery kinetics (90 s and 60 s), outstanding selectivity over several interferential gases and good stability tested in 3 months. In addition, the sensor could detect ethanol at a low detection limit (<10 ppm), which exhibited good reproducibility. The high ethanol gas sensing performance of the Co_3O_4 NRs can be explained by a typical *p*-type behavior with the one-dimension structure, nano-porosity, large specific surface area, good crystallinity and the open space of nanorod arrays.

1. Introduction

Cobalt oxide (Co_3O_4) is considered to be one of the most representative *p*-type semiconductors and the most promising functional materials in many technological areas, such as heterogeneous catalysis, supercapacitors, lithium-ion batteries, and especially gas sensors [1–5]. In view of these profitable utilizations, a large number of efforts have been focused on the synthetic techniques of growing cobalt oxide nanostructures, including hydrothermal, electrospinning, chemical vapor deposition, sputtering and pulsed laser deposition, etc. [6–9]. Various nanostructures on synthesizing Co_3O_4 for gas detection were reported, such as meso- and macroporous Co_3O_4 nanorods for effective volatile organic compounds gas sensing [10], concave Co_3O_4 octahedral mesocrystal for formaldehyde and ethanol detection [11], and Co_3O_4 hollow nanospheres toward toluene and acetone vapors [12]. From the viewpoint of device structure, Co_3O_4 gas sensors have been usually synthesized in the form of thin films, in which the powders are screen printed on prefabricated electrodes ceramics tubes or insulative plates followed by annealing at the appropriate temperature. Nevertheless, only a small fraction of the species adsorbed near the grain boundaries in thin-film gas sensors is active in modifying the electrical transport properties, which are apt to lose the characteristic advantage of the larger length-to-diameter and surface-to-volume ratios than bulk materials and films for nanostructure building blocks resulting from agglomeration [13]. There is thus still an evident need for detailed investigations regarding the device structures.

On the other hand, the gas sensing performance of Co_3O_4 for ethanol detection which is closely related to the issues of public health and safety has been arousing great interest. Previously, Choi et al. have discussed that the gas responses of various Co_3O_4 nanostructures such as nanorods, nanosheets, and nanocubes to 100 ppm C_2H_5OH at 300 °C were several times higher than those of the Co_3O_4 agglomerated nanopowders, respectively [14]. Cao et al. have synthesized Co_3O_4 with different morphologies which exhibited high performance at an operating temperature of 300 °C as an ethanol sensor [15]. Yoon et al. have fabricated the Co_3O_4 nanofibers which exhibited high responses (~51.2) to 100 ppm C_2H_5OH at 301 °C [16]. All the above sensors have the optimal working temperatures at about 300 °C, which is too high for practical application. A large scale monodisperse porous flowerlike Co_3O_4 microspheres consisting of nanoplatelets showed enhanced ethanol sensitivity and selectivity at a relatively low temperature of 135 °C, however, with a low gas response at ~15 for 500 ppm ethanol [17]. Thus, fabricating gas sensors to ethanol based on Co_3O_4 which have high response at a low temperature is an uphill task. Nanoarray-based sensors are of particular interest because

* Corresponding author. Tel.: +86 571 87953139; fax: +86 571 87952625.
E-mail address: zlp1@zju.edu.cn (L. Zhu).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.05.093

of not only low cost and great miniaturization potential, but also high reaction rate, which leads to a higher sensing performance. So far, huge amounts of works were focused on the *n*-type metal oxide semiconductor nanoarray-based gas sensors (e.g. ZnO, SnO_2, TiO_2) and most of the experimental and theoretical knowledge was focused on the *n*-type case [18–21]. Few works have dealt with *p*-type semiconducting metal oxide array-based gas sensors. Thus, exploring the gas sensing performance arising from the nanostructure arrays of *p*-type semiconductors is demanding.

Herein, we present the fabrication of the rhombus-shaped Co_3O_4 NR array-based gas sensor with high-performance for ethanol detection, whose fabrication process does not require expensive and complicated fabrication techniques. The characterization of the NR arrays was investigated by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopies (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The NR arrays directly grow on the supporting substrates and intensive contact with the substrate supplies a simple method to prepare a nanoarray-based gas sensor without the conventional film formation process. Subsequently, the high-performance sensing properties of the porous Co_3O_4 NR arrays for ethanol gas and the gas-sensing mechanism will also be discussed.

2. Experimental

2.1. Synthesis

The process of preparing cobalt hydroxide was greatly simplified from our previous method [22]. All chemicals were of analytical grade and used as purchased without further purification. The typical experiments were as follow and the fabricating process is illustrated in Fig. 1(a): 4 mmol (1.16 g) of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), 8 mmol (0.29 g) of ammonium fluoride (NH_4F) and 8 mmol (1.12 g) of hexamethylenetetramine ($C_6H_{12}N_4$, HMT) were dissolved in 40 ml high purity water (18.3 MΩ cm resistivity) under stirring at room temperature. After stirring for 10 min, the homogeneous solution was transferred into a 50 ml Teflon-lined stainless steel autoclave. Then, a piece of cleaned polycrystalline alumina ceramics plate (13 mm × 7 mm, 0.5 mm in thick) which have been plated Ag-Pd finger regions (five pairs, both the width and distance are 200 μm) as electrodes were immersed in the reaction solution against the inner wall of the autoclave and fixed by polyimide tapes. The autoclave was sealed and maintained at 95 °C for 24 h inside an electric oven. After cooling down to room temperature spontaneously, the substrate was removed, rinsed with distilled water several times in order to remove the free nanoparticle debris and the residual reactant, and dried at 60 °C under vacuum for 2 h. Finally, the as-prepared pink precursors were converted to Co_3O_4 via thermal decomposition after annealing at 450 °C in air for 4 h with a heating rate of 10 °C per minute. The obtained samples could be directly used for gas sensing measurements, and a top view of sensor substrate and the samples before and after annealing are shown in Fig. 1(b).

2.2. Characterization

The crystal phase identification were investigated by X-ray diffraction (XRD, Bede D1) system with Cu-$K_{\alpha1}$ radiation (λ = 0.15406 nm) over the 2θ range of 10–80°. The morphologies of both the precursor and calcined products were investigated using field emission scanning electron microscopy (FESEM, Hitachi S-4800) with an accelerating voltage of 5 kV. Further structural analysis of individual NR was carried out using high-resolution transmission electron microscopy (HRTEM, FEI F20) with an accelerating voltage of 200 kV. Fourier transform infrared spectroscopy (FTIR, TENSOR 27) was characterized with DTGS detector by making pellets with KBr powder. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) measurement was performed with a monochromatic Al-Kα ($h\nu$ = 1486.6 eV) X-ray source. The electrical characteristics were measured at room temperature in the dark using a semiconductor parameter analyzer (Agilent E5270B) with the bias voltage range of −10 to 10 V.

2.3. Gas-sensing measurements

The gas-sensing properties of the Co_3O_4 sensors were performed on an intelligent gas sensing analysis system (CGS-1TP, Beijing Elite Tech Co., Ltd, China). The analysis system offered an external temperature control (from room temperature to 500 °C), which could conductively adjust the sensor temperature with a precision of 1 °C. The sensors were laid on the temperature control and pre-heated at different operating temperatures for about 30 min. Two probes were pressed on sensor electrodes by controlling the position adjustment in the analysis system. When the resistance of the sensor was stable, saturated target gas was injected into the

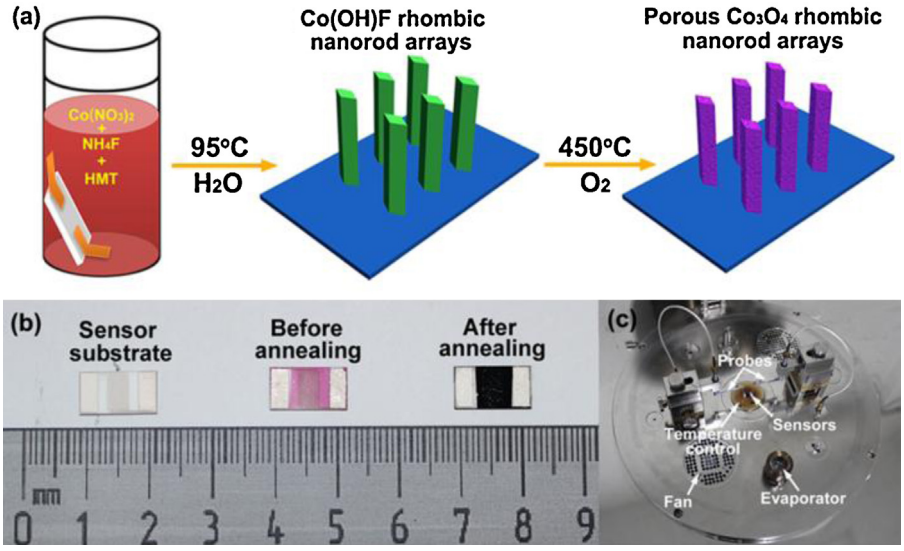

Fig. 1. (a) Schematic diagram of the fabricating process. (b) Top view of sensor substrate and sample sensors. (c) A photograph of the gas sensing analysis system.