Journal of Alloys and Compounds 704 (2017) 117–123

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

In-situ deposited ZnO film-based sensor with controlled microstructure and exposed facet for high H_2 sensitivity

Xiaonan Wu, Shunshun Xiong, Zhenghao Mao, Youjin Gong, Wei Li, Boyu Liu, Sheng Hu, Xinggui Long*

Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, Sichuan, 621900, PR China

ARTICLE INFO

Article history:
Received 29 December 2016
Received in revised form
3 February 2017
Accepted 5 February 2017
Available online 8 February 2017

Keywords:
ZnO sensor
In-situ growth
Microstructure
Oxygen vacancies

ABSTRACT

A facile in-situ solution deposition method is used to fabricate ZnO film-based sensors with controlled microstructures and exposed facets. Three kinds of ZnO film-based sensors with different microstructures and exposed facets were grown on the $KMnO_4$-activated electrode substrates by adjusting the supersaturation level of deposition solution. Among them, the tower-like ZnO film-based sensor with large (0001) exposed area exhibits a high H_2 sensitivity, which is attributed to its abundant oxygen vacancy defects. Moreover, it is found that a proper annealing treatment for the tower-like ZnO film-based sensor increases its oxygen vacancies. The H_2 response value of the annealed tower-like ZnO sensor is 2 times higher than that of the non-annealed sensor, and the stability of the sensor is retained after the annealing treatment.

1. Introduction

Semiconductor metal oxide based gas sensors play an important role in detecting explosive or toxic gases for industrial production, environment monitoring, chemical process controlling and personal safety [1]. The sensing mechanism involves the adsorption of gas molecules on the surface of metal oxide sensing materials that causes the change of their resistivity [2]. Recently, nano-scaled metal oxide sensors have attracted much attention because of their high specific surface areas, which significantly increase gas adsorption sites [3].

Nano-scaled ZnO is an ideal candidate for gas sensors, due to its manifold nanostructures and excellent semiconductor properties [4]. Substantial effort has been done to design the ZnO sensors with various nanostructures. One-dimensional (1D) ZnO nanostructures, such as nanorods [5], nanowires [6] and nanofibers [7], have showed great potential in enhancing the sensitivity of ZnO sensors due to their ultrahigh surface-to-volume ratios. Furthermore, some studies indicate that the different exposed facets of ZnO nanostructures have a remarkable influence on the sensitivity of ZnO sensors. Because the difference of surface atom structures of exposed facets could cause a distinct ability to absorb the gas molecules [8,9].

However, fabrication of ZnO sensors with well-designed microstructures and exposed facets is still challenging. The common fabrication process of ZnO nano-sensors is based on the preliminary synthesis of ZnO nanostructures and the following dip coating of the products on the ceramic tubes [9,10]. In this manner, the initial obtained structure is hard to be preserved in the sensor and the expected excellent sensing response is diminished [8]. In order to solve this problem, the in-situ fabrication methods including chemical vapor deposition (CVD) [11], electrospinning deposition [7] and sputtering [12], are employed on the deposition of 1D ZnO films to obtain the planar film-based ZnO sensors, although instrumental complexity poses high investment costs [13,14]. In this regard, low cost non-vacuum solution based methods are appealed for the preparation of the ZnO film-based sensors. A prior-deposited seed layer is often necessary for the deposition of 1D ZnO films on the substrates through chemical solution approaches, however, the seed layer may disturb the sensing response [5,15–17]. The seed-free solution methods need to be developed. In addition, to the best of our knowledge, the in-situ fabrication of ZnO film-based sensors with controlled exposed facets by a direct solution deposition process has not been reported.

In this work, a seed-free solution deposition method was initiated to fabricate ZnO film-based sensor with definite exposed

* Corresponding author.
E-mail address: xingguil@caep.cn (X. Long).

http://dx.doi.org/10.1016/j.jallcom.2017.02.040
0925-8388/

facets. Three kinds of ZnO film-based sensors were in situ grown on the $KMnO_4$-activated electrode substrates. The microstructures and exposed facets of the ZnO films were controlled by adjusting the supersaturation level of deposition solution. The H_2 sensing properties of the obtained sensors were investigated. The tower-like ZnO film-based sensor which possessed a large (0001) exposed area showed a high H_2 sensitivity. Our work would provide a facile route to prepare controlled-nanostructures ZnO film-based sensors.

2. Material and methods

2.1. Materials

Potassium permanganate ($KMnO_4$), n-butanol, zinc acetate dihydrate ($ZnAc_2 \cdot 2H_2O$), ammonia ($NH_3 \cdot H_2O$) and ethanolamine (MEA) were used as received from commercial suppliers without further purification. Electrode substrates were supplied by Huachuang Ruike Science and Technology Wuhan Co., Ltd. The electrode slice was prepared based on the alumina substrate (30 × 6 mm). The platinum paste was printed by screen printing onto the alumina substrates. The gap between the gear shaping electrodes was 0.42 mm.

2.2. Preparation of ZnO film-based sensors

The ZnO sensing films were in situ grown on the electrode substrates. The electrode substrates were placed in a vial filled with 5 mM fresh $KMnO_4$ solution and 1.3 mM *n*-butanol (as the reducing agent for $KMnO_4$) [18]. The closed vial was placed in a water bath at 90 °C for activating the substrates. After 15 min, the substrates were moved out and washed with the deionized water. Meanwhile, 1.4–2.2 mol MEA was added into 0.08 M $ZnAc_2 \cdot 2H_2O$ solution and $NH_3 \cdot H_2O$ was used to control the solution PH near 11.5. Then the activated substrates were obliquely inserted into the solution at 90 °C for growing ZnO films. The film-coated substrates were taken out after 1 h and washed with ethanol.

2.3. Characterization

Powder X-ray diffractometer (XRD, PANalytical X'Pert MRD) with Cu Kα-radiation was used to measure the crystalline structure of the films. The field-emission scanning electron microscope (FE-SEM, Zeiss-Ultra 55) and the high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30) were used to characterize the morphology and microstructure. The Hitachi F-7000 spectrometer was used to measure the room temperature photoluminescence (PL) spectra with an excitation wavelength of 325 nm. The surface compositions of the samples were characterized by a Perkin-Elmer PHI-5702 multi-functional X-ray photoelectron spectroscopy (XPS) with Al Kα radiation.

2.4. Gas sensing measurements

The CGS-4TP intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China) was used to measure the gas sensing properties of the sensors. The concentrations of H_2 were controlled by changing the mixing ratio of drying air and dry air-balanced analyte gas using mass flow controllers. The H_2 response of the sensors was defined as Ra/Rg, where Ra and Rg were the resistances measured in the absence and presence of H_2.

3. Results and discussion

A typical 1D nanorod-morphology was observed in the SEM image of ZnO film-based sensors depositing on the $KMnO_4$-activated electrode substrates (Fig. 1a). However, only some non-regular ZnO scattered on the non-activated substrates (Fig. 1b). Obviously, the $KMnO_4$ activation treatment was effective for the in-situ growth of ZnO nanorods films on the electrode substrates. When the electrode substrates were soaked with the $KMnO_4$ solution, $KMnO_4$ produced small amounts of Mn(O)OH on the substrates and the Mn(O)OH could serve as the heterogeneous nucleation centers of ZnO crystal [18,19]. As shown in Fig. 1c, no obvious seed layer was found in the cross-section image of ZnO nanorods film-based sensors. Both the vertical and inclined nanorods were grown on the surface of electrode substrates. Such configuration ensured the nanorods were cross-linked, which could provide a continuous path for the current flowing in the gas

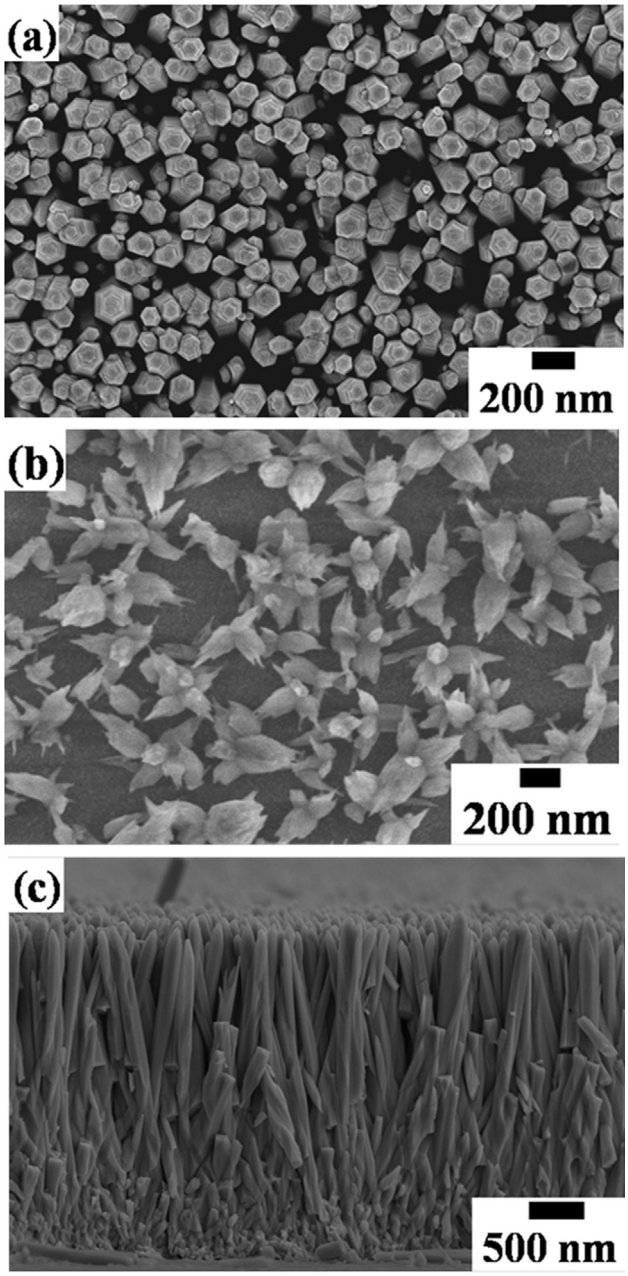

Fig. 1. SEM images of the ZnO film-based sensors (a) deposited on the $KMnO_4$-activated electrode substrates and (b) deposited on the non-activated electrode substrates. (c) Corresponding cross-section image of (a).