Sensors and Actuators B 199 (2014) 403–409

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Ni-doped ZnO nanorods gas sensor: Enhanced gas-sensing properties, AC and DC electrical behaviors

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ARTICLE INFO

Article history:
Received 26 December 2013
Received in revised form 4 March 2014
Accepted 28 March 2014
Available online 6 April 2014

Keywords:
ZnO
Doping
Gas-sensing
Current–voltage curve
AC impedance spectroscopy

ABSTRACT

Ni-doped zinc oxide (ZnO) nanorods had been successfully fabricated via a fast microwave-assisted hydrothermal synthesis at 150 °C. The morphology and composition were carefully characterized by X-ray diffraction, field emission scanning electronic microscopy, and transmission electron microscopy. Gas-sensing testing results demonstrated that Ni-doped ZnO nanorods had enhanced gas-sensing performance. Furthermore, AC impedance spectroscopy and DC current–voltage curves were observed to investigate the gas-sensing mechanism. Current–voltage curves are approximately close to a linear function, indicating the potential barriers formed at the electron-depleted surface layer occupy a dominant when carriers transport in the gas sensor, and AC impedance spectra indicates the potential barriers height of the electron-depleted surface layer.

1. Introduction

Recently, metal oxide semiconductor gas sensors are among the most widely researched and used gas sensors due to their advantageous features, such as high sensitivity under ambient conditions, low power consumption, low price, prompt response and simple structure. A large number of semiconductor oxides such as TiO_2 [1,2], SnO_2 [3,4], ZnO [5–7], NiO [8,9], and Fe_2O_3 [10,11] have been proven to be effective gas sensor materials. However, metal oxide semiconductor gas sensors have some deficiencies, such as: poor thermal stability, reliability, selectivity, anti-interference and high working temperatures, which limit the further development and widely application of metal oxide gas sensors. At present, numerous efforts have been made to improve the sensing properties of metal oxide semiconductor gas sensors, among which, the strategy of doping modification with various metallic elements, for example, noble metal [12], rare-earth metal [13,14], transition metal [4,15–17], and metal oxide [18], had been proven effective.

Meanwhile, metal oxide semiconductors are promising candidates for gas sensor development and have received a majority of attention in recent decades. However, the fundamental understanding of sensing mechanism remains poor since an empirical optimization of gas-sensing performance has always been the investigation focus. To meet the demands for gas sensors which are capable of detecting environmentally important gases within sub-ppb levels, a more fundamental basis understanding the gas-sensing mechanism is necessary. The working principle of a typical resistive gas-sensor material is based on a shift of the state of equilibrium of the surface oxygen reaction due to the presence of the target gas. The resulting evolution in chemisorbed oxygen is recorded as a change in resistance of the sensor material [19–22]. However, the change of resistance cannot reflect the real working process of the gas sensor. It is well known that AC impedance spectroscopy, DC resistance and current–voltage (I–V) characteristics have usually been used to analyze the electrical process [23,24], for example, the charge carriers translation, potential barriers [25]. Therefore, may be can they be applied to understand the gas-sensing mechanism.

In this paper, we report an economical method for preparing Ni-doped ZnO nanorods. The morphology, structure, and gas sensing performance were carefully investigated. AC impedance spectroscopy and DC resistance, I–V characteristics were observed to analysis the gas-sensing mechanism. Furthermore, we expected such a gas senor based on Ni-doped ZnO nanorods could be reliably used for detection of inflammable gases.

2. Experimental

2.1. Synthesis

All the chemicals are of analytical reagent (AR) grade used without further purification, and purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China). Zinc nitrate hexahydrate

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http://dx.doi.org/10.1016/j.snb.2014.03.108
0925-4005/

($Zn(NO_3)_2{\cdot}6H_2O$), nickel acetate tetrahydrate ($Ni(Ac)_2{\cdot}4H_2O$) D-(+)-glucose ($C_6H_{12}O_6{\cdot}H_2O$), hexamethylene tetramine (HMTA), and urea.

In a typical procedure, 2.5 mmol of $Zn(NO_3)_2{\cdot}6H_2O$, 2 mmol of HMTA, 3.6 mmol of $C_6H_{12}O_6{\cdot}H_2O$ and 1.25 mmol of urea were successively introduced into 40 mL deionized water while stirring for 10 min at room temperature. Then, 0, 0.125, 0.167, 0.25, 0.5, 2.5 mmol of $Ni(Ac)_2{\cdot}4H_2O$ were added to solution, respectively. After being vigorously stirred for another 30 min at room temperature, the as-obtained mixture was transferred to a Teflon vessel of the MDS-6 (Microwave Digestion/Extraction System, Shanghai Sineo Microwave Chemical Technology Co. Ltd.). With a programmable temperature control, the desired reaction temperature was established to 150 °C. The as-prepared powders were collected by centrifugation, rinsed several times with deionized water and pure ethanol, and then, vacuum-dried at 80 °C for 8 h. Finally, the samples were obtained by calcining the precursor at 500 °C for 2 h in air.

2.2. Characterization

The phase identification of the as-obtained samples was performed by X-ray diffraction (XRD; X'pert, Philips, Holland) with Cu Kα1 radiation ($\lambda = 1.5406$ Å) at 40 kV, and 30 mA over the 2θ of range 15–75°. The morphology and microstructure were carried out by using field emission scanning electronic microscopy (FE-SEM; JSM-6701F, JEOL, Japan). Transmission electron microscopy (TEM; JEM-3010, Questar, New Hope, USA), high-resolution transmission electron microscopy (HRTEM) images combined with select area electron diffraction (SAED) and energy dispersive spectroscopy (EDS; FeatureMax, Oxford Instruments, Abingdon Oxfordshire, UK) were recorded on a FEI TecnaiF30G2 field emission microscope, operating at an acceleration voltage of 300 kV. The DC electric conductivity was measured by using a high resistance meter (4339B, Agilent, Santa Clara, CA, USA). AC impedance spectroscopy was performed using an Impedance Analyzer (4294A, Agilent, CA, USA) in the 100 Hz–1 MHz frequency range. *I–V* characteristics were measured using a Keithley instruments (Model 2410, Sourcemeter, Cleveland, USA) in the voltage range from −20 V to 20 V with a heating temperature varying from room temperature to 400 °C.

2.3. Sensor fabrication and measurements

The structure of the gas sensor belongs to side-heated type, and the basic fabricated process is as follows. The as-obtained Ni-doped ZnO nanorods were mixed and grinded with some terpineol adhesive in an agate mortar to form gas-sensing paste. The paste used as sensitive body was coated on a ceramic tube with Au electrodes and platinum wires, and then sintered at 500 °C for 2 h to remove the binder. A Ni–Cr alloy crossing the ceramic tube was used as a heating resistor which is controlled by heating voltage V_h to ensure both substrate heating and temperature controlling. In order to improve their stability and repeatability, the gas sensors were aged at 300 °C for 10 days in air. The gas-sensing properties were tested using a gas

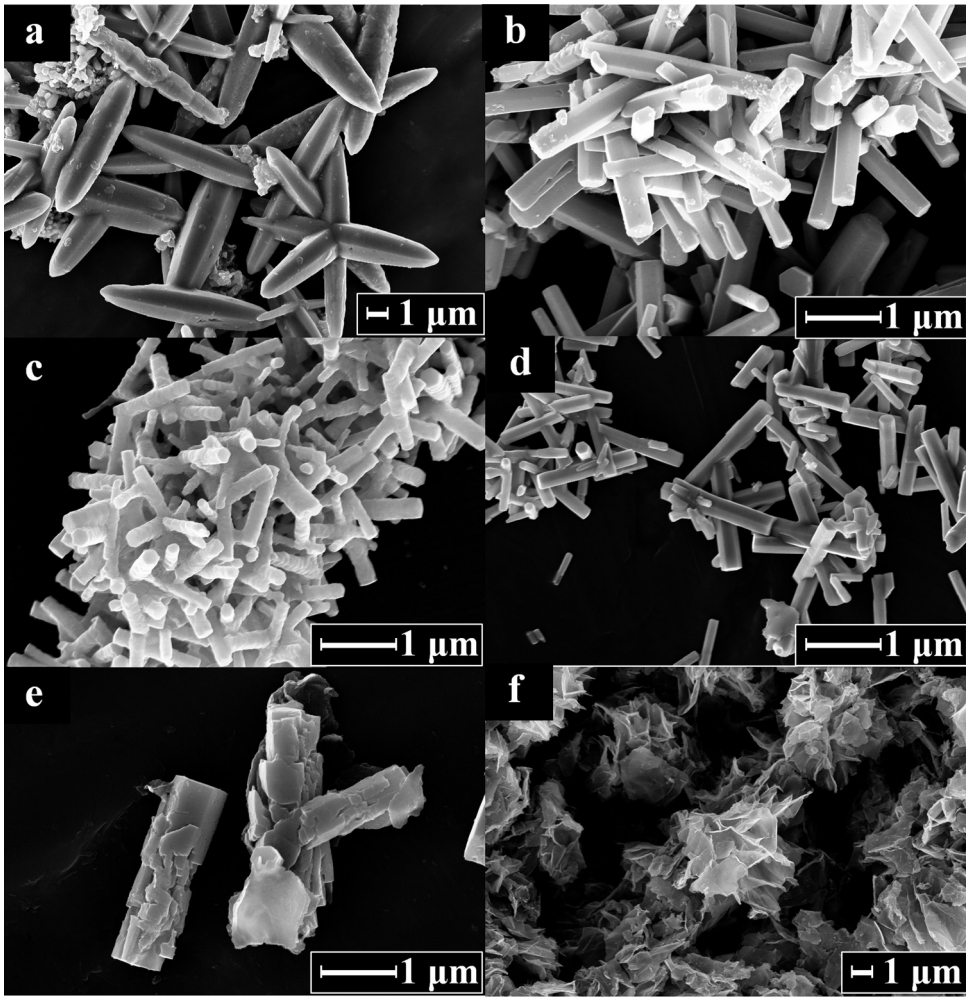

Fig. 1. Typical SEM images of S1, S2, S3, S4, S5, S6.