Sensors and Actuators B 224 (2016) 153–158

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Enhanced H_2S gas sensing properties of undoped ZnO nanocrystalline films from QDs by low-temperature processing

Jianfeng Deng[b], Qiuyun Fu[a,b,*], Wei Luo[b], Xiaohu Tong[b], Jiahui Xiong[b], Yunxiang Hu[b], Zhiping Zheng[b]

[a] State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, PR China
[b] School of Optical and Electronic Information, Huazhong University of Science & Technology, No. 1037 Luoyu Road, Hongshan, Wuhan 430074, PR China

A R T I C L E I N F O

Article history:
Received 31 August 2015
Received in revised form 7 October 2015
Accepted 10 October 2015
Available online 22 October 2015

Keywords:
Gas sensors
ZnO QDs
H_2S

A B S T R A C T

H_2S gas sensitive films based on ZnO QDs of 3.8 nm were prepared through a spin-coating process. The sensitivity of ZnO films was greatly improved after low-temperature processing and grain sizes remained below twice Debye length. A modified flat band diagram was proposed to explain this great improvement. The comparison of responses of ZnO films annealed at different temperatures was made and the sensors exhibited quick response and recovery. The response of ZnO films toward H_2S of 68.5 ppm was a relatively high value of 75 at room temperature, which reached its highest value of 567 at 90 °C. The optimal operating temperature of 90 °C is relatively low compared to other gas sensors based on ZnO. Meanwhile, ZnO films showed good selectivity toward H_2S against SO_2, NO_2 and NH_3.

1. Introduction

Hydrogen sulfide (H_2S) is a highly toxic, flammable and colorless gas and it is also known to be a major contributor to acid rain when oxidized in the atmosphere to SO_2 [1]. Therefore, gas sensors capable of sensitively and selectively detecting low concentrations of H_2S are important for human safety and environment. Semiconductors such as ZnO, SnO_2, In_2O_3, CeO_2, and WO_3 are widely used in gas sensors to H_2S based on the changes of their electrical resistance on exposure to H_2S and air [2–4]. Among these metal oxides, ZnO, a nontoxic, inexpensive, and chemically stable n-type semiconductor, has been proven to be an excellent gas sensing material for the detection of both toxic and combustible gases [5–7]. Various forms of ZnO nanostructures have been synthesized, including nanoparticles [8], nanowires [9], nanorods [10], nanobelts [11]. However, most researchers reported gas sensors based on ZnO toward H_2S operating at high temperatures, which requires a complex structural design and fabrication process for the sensors [12–16]. Kaur et al. [13] reported H_2S sensors based on CuO functionalized ZnO nanotetrapods operating at room temperature, but the response of the sensors to 100 ppm H_2S was only 40. Improving sensitivity and decreasing operating temperature of gas sensors are desirable for detecting lower concentration gas and expanding their applications.

Quantum dots (QDs) with extremely small size, large and sensitive surface are suggested promising for constructing fast and sensitive gas sensors. The QDs with lots of unsaturated bond and high surface energy are apt to absorb gas molecules and therefore its operating temperature decreased [17]. When the grain size is smaller than twice Debye length (L_D), grain size becomes one of the most important factors for the sensor response. Theoretically the response increases with the decrease of the grain size [18–20]. However, when the grain size is comparable to quantum size, the sensor showed poor response to gases [21,22]. Some researchers tried to improve the sensitivity of the sensor based on QDs using the chemical doping methods or composite structure in their research, but the sensitivity of the sensors did not improved too much [23,24].

In this work, the gas sensitive films based on ZnO QDs have been prepared through wet chemical method on alumina thin flats substrates. The response to gases of ZnO films as synthesized was also poor. Such ZnO films showed high resistance, which indicated poor electron transportation. Therefore samples were annealed at low temperatures to improve their conductivities. In addition, the average grain size was kept no more than $2L_D$ because the thermal processes were performed at low temperatures. The sensitivity of ZnO films increased greatly and meanwhile the films showed high selectivity toward to H_2S gas. The optimal operating temperature

* Corresponding author at: State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, No.1037 Luoyu Road, Hongshan, Wuhan 430074, PR China.
E-mail address: fuqy@mail.hust.edu.cn (Q. Fu).

http://dx.doi.org/10.1016/j.snb.2015.10.022
0925-4005/

was about 90 °C and lower than gas sensors based on other ZnO nanostructures. Even at room temperature, the film also showed good sensitivity. A modified flat band diagram is proposed to explain the underlying mechanism.

2. Experimental

2.1. Synthesis of ZnO QDs

ZnO QDs were synthesized via a colloidal procedure [25]. All chemical reagents were analytical grade without further purification and treatment. $Zn(OAc)_2{\cdot}2H_2O$ (15 mM) in 100 mL anhydrous ethanol was refluxed at 80 °C for 3 h with continuous stirring. After that, the solution was cooled down to 0 °C in ice water, and the zinc acetate solution was obtained. Meanwhile, $LiOH{\cdot}H_2O$ (18 mM) was dissolved into 50 mL anhydrous ethanol to obtain LiOH solution. Then the above two solutions were mixed by continuous stirring for 10 min to obtain a transparent and colorless solution containing ZnO QDs. Zinc acetate reacted with Lithium hydroxide as follows:

$$Zn(CH_3CO_2)_2 + 2LiOH \rightarrow ZnO + H_2O + 2LiCH_3CO_2 \quad (1)$$

300 mL N-hexane was added into the solution and then ZnO precipitated as white products. ZnO precipitant was separated from solution through centrifugation and then was repeatedly washed with anhydrous ethanol and N-hexane to remove the remaining ions in the precipitation. Next, ZnO precipitation was dispersed into anhydrous ethanol and finally ZnO QDs solution with concentration of 40 mg/mL was obtained.

2.2. Fabrication of ZnO films

ZnO films fabrication was carried out at room temperature using spin-coating method published in our former paper [26]. Alumina thin flats (with dimension ca. 10 mm × 12 mm) preprinted with Ag interdigital electrodes were used as the sensor substrate. Typically, 100 μL ZnO QDs solution were dropped onto the pre-cleaned substrate and spin-coated at 2500 rpm for 20 s, then this procedure was repeated twice to get a three-layer ZnO QDs film. Samples were then annealed at low temperature (200 °C, 300 °C) and the duration of annealing was 1 h.

2.3. Gas sensing performance testing setup

Gas sensing properties were tested in a closed chamber of 7.3 L volume with controlled temperature and humidity. All gas sensing tests throughout the work were performed under atmospheric pressure with the same relative humidity of (50 ± 1)%. The static method was employed in the gas sensing test. The gas concentration was calculated in ppm, which was determined by the volume ratio of the injected gas to air under standard atmospheric pressure. First, the test chamber was filled with air and the corresponding resistance of ZnO film in air (R_{air}) was measured. Then the target gas was injected into the chamber and filled quickly the whole chamber. Next, the resistance changes of ZnO films in the presence of the target gas (R_{gas}) were recorded. Finally, the response (S) of ZnO film to H_2S was as calculated through $S = R_{air}/R_{gas}$.

2.4. Characterization techniques

UV–vis absorption spectra of the ZnO QDs solution were recorded by a Shimadzu UV-2500 UV–visible photospectrometer (Shimadzu Co., Japan). The phase identification and crystalline structures of ZnO QDs powders and ZnO thin films deposited on the alumina substrates were analyzed by X-ray diffraction (XRD) using PANalytical B.V. X'Pert PRO X-ray diffractometer with Cu Kα radiation of 1.5406 Å operated at 40 kV and 40 mA. Transmission electron microscope (TEM) images were obtained from a JEOL2100 microscope (JEOL, Japan). The thickness of the film was measured by a Step Profiler.

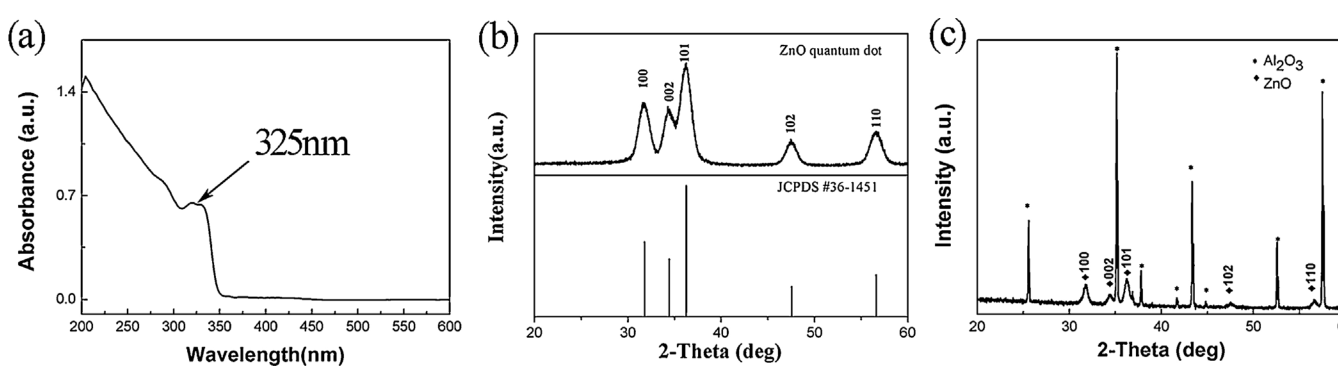

Fig. 1. (a) XRD patterns and (b) UV–vis absorption spectrum of the as-synthesized ZnO QDs. (c) XRD patterns of ZnO films on Al_2O_3 substrate annealed at 300 °C.

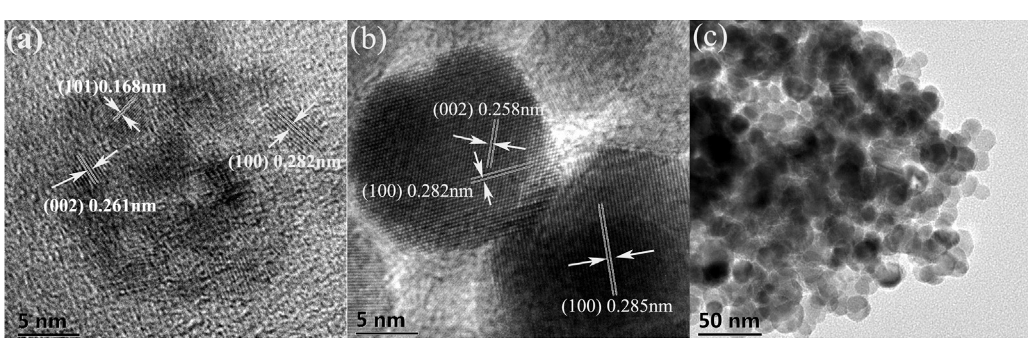

Fig. 2. TEM images of ZnO films (a) without annealing. (b) and (c) annealed at 300 °C.