Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 4749–4756

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Influence of annealing on the structural, optical and photoluminescence properties of ZnO thin films for enhanced H_2 sensing application

K. Vijayalakshmi*, K. Karthick, D. Gopalakrishna

PG and Research Department of Physics, Bishop Heber College, Tiruchirappalli, Tamil Nadu, India

Received 6 October 2012; received in revised form 19 November 2012; accepted 20 November 2012
Available online 27 November 2012

Abstract

Nanostructured zinc oxide (ZnO) thin film sensors were prepared by spray pyrolysis, and their structural, optical, photoluminescence and morphological properties were investigated by X-ray diffractometer, UV–vis spectrometer, photoluminescence spectrometer, and scanning electron microscope (SEM), respectively. The post-annealing of ZnO film in air at 400 °C was found to be effective for the distribution of grains and their sizes, which favors the *c*-axis orientation of the film. This enhancement is accompanied by an increase in the optical band gap from 3.4 eV to 3.53 eV, which confirms the uniformity of ZnO film prepared by using a specially designed spray nozzle. SEM micrograph after heat treatment revealed uniform distribution of particles with well grown grains of ZnO. Hydrogen sensing measurement indicated the annealed ZnO film to show much higher response than the as deposited film. To understand the enhancement of the sensing performance of the annealed ZnO film, the gas sensing mechanism of the film was proposed and discussed. The magnitudes of the sensor response as well as its dependence on annealing differ significantly depending on the crystallite size of the film.

Keywords: C. Optical properties; ZnO thin films; Annealing; H_2 gas sensor

1. Introduction

One of the most critical needs in gas sensing is to develop low cost and portable hydrogen sensors that are able to selectively detect hydrogen gas near room temperature [1]. At present, commercial hydrogen detectors are not suitable for widespread use, as they are too bulky, expensive, and some are dangerous. The sensors working at high temperature themselves become a possible trigger of explosion due to the high input of electric energy for sensor operation. From the point of view of safety with the global environment, the present work has been realized with the necessity to develop hydrogen sensors working at low temperature. Recently, the main effort of H_2 sensor development has been the improvement of H_2 gas sensitivity as well as selectivity, and to decrease the operating temperature. Semiconducting metal oxide sensors, due to their small dimensions, low cost and high compatibility with microelectronic processing, have been widely investigated to meet the requirement of H_2 detection. Among various kinds of semiconducting metal oxide materials, zinc oxide (ZnO) is one of the pioneers and most promising H_2 sensing materials, due to its high chemical stability and easy fabrication [2,3].

ZnO is an n-type semiconductor of wurtzite structure with a large band gap energy of 3.37 eV at low temperature, and 3.3 eV at room temperature [4,5]. Its usefulness as a hydrogen sensor material was first realized after Seiyama et al. [6] demonstrated the detection of inflammable town gases by ZnO film. The physical properties of ZnO depend on the microstructure of the material, including crystal size, morphology, orientation, aspect ratio and crystalline density [7]. Sensing properties of ZnO are directly related to its preparation history, particle size, morphology and operating temperature. Many different methods such as RF/DC sputtering [8,9], sol–gel [10], metal organic chemical vapor deposition [11], and pulsed laser deposition [12] were used for the preparation of ZnO films. The spray pyrolysis technique was used extensively in

*Corresponding author. Tel.: +91 9994647287 (mobile).
E-mail address: viji71naveen@yahoo.com (K. Vijayalakshmi).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.11.061

depositing metal oxide films [13]. The technique has excellent features such as being easy, low cost and simple, as no sophisticated equipment is required. The film produced with spray pyrolysis is inherently uniform and the surface to volume ratio of the nano drops is very large, making them very receptive to heat treatment and pyrolysis [14]. The film thickness and stoichiometry are easy to control in this technique, and the resulting film is well compacted [15]. In the present work, the ZnO films were deposited by spray pyrolysis on a glass substrate kept at a temperature of 300 °C, and subsequently annealed at 400 °C for 1 h. The effect of annealing on the structural, morphological, optical, photoluminescence and H_2 sensing properties of the film was investigated.

2. Experimental details

ZnO thin films were deposited onto the glass substrate using 0.1 M concentration of aqueous solution of zinc acetate. To prepare 100 ml precursor solution, the required quantity of salt is dissolved in double distilled water. Before deposition, the substrates were cleaned in chromic acid and potassium dichromate in a liter of concentrated sulfuric acid. During synthesis, various preparative parameters like solution spray rate, nozzle to substrate distance, carrier gas flow rate, etc. were optimized in order to obtain transparent, uniform, adherent and pinhole free deposits. The deposition parameters used for the preparation of ZnO thin films in the present study are summarized in Table 1. Compressed air was used to atomize the solution containing the precursor compounds through a spray nozzle over the preheated substrate. The substrate holder was equipped with a thermocouple, heating element and a temperature controller. The spray nozzle is specially designed with two concentric glass pipes. Through the inner pipe flows the solution and between the inner and outer, the air stream; the spray was produced by the Ventury effect at the end of both pipes. Hazardous fumes evolving at the time of deposition were sucked out using an external exhaust system connected to the deposition chamber. The schematic diagram of the spray pyrolysis unit is shown in Fig. 1.

Table 1
Summary of deposition parameters for ZnO thin films.

Parameter	Values
Substrate temperature	300 °C
Solution feeding rate	3 ml/min
Carrier gas flow rate	0.4 kg/cm^2
Precursor concentration	0.1 M
Precursor Volume	100 M
Solvent	Water
Nozzle to substrate distance	30 cm
Deposition time	10 min
Temperature of annealing	400 °C

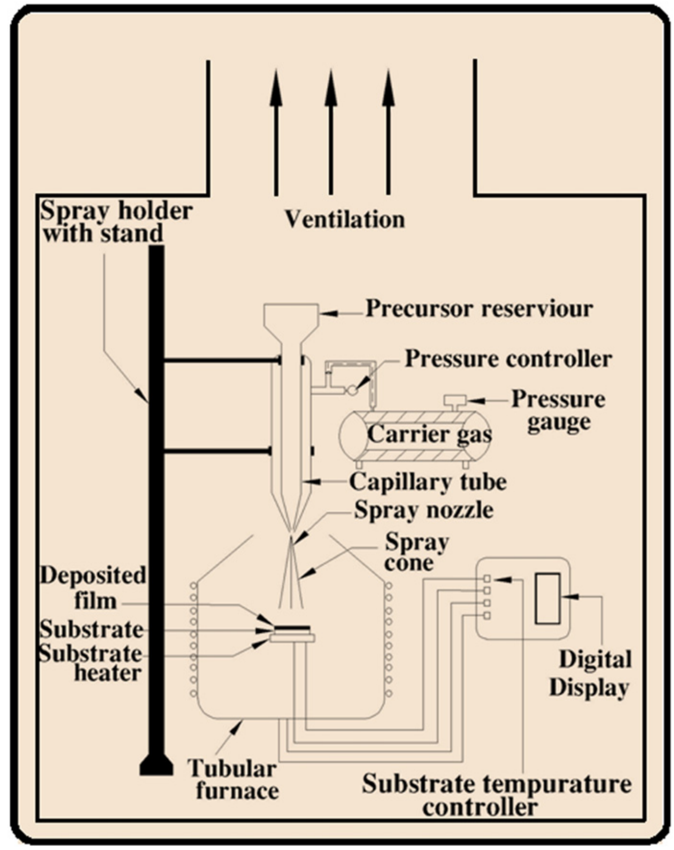

Fig. 1. Schematic of the experimental setup used for the spray pyrolysis deposition technique.

When the aqueous solution of zinc acetate was sprayed over the hot substrate, fine droplets of solution thermally decomposed after falling over the hot surface of the substrate. This resulted in the formation of a well adherent and uniform ZnO film. Rapid thermal annealing for 1 h at 400 °C after deposition determined desorption of the large number of chemisorbed oxygen species at the surface of freshly prepared ZnO film. The loss of adsorbed oxygen increased the electrons concentration of the surface and improved the conductance. These films were further used to investigate the structural, optical and photoluminescence properties. The structural characterization was carried out using an X Perto X-ray diffractometer with CuKα radiation, and optical characterization using a UV–vis Lambda-35 Spectrophotometer over the wavelength range 350–850 nm. Photoluminescence (PL) studies were carried out using a Varian Carry Eclipse PL spectrophotometer. The morphology of the films was studied using a HITACHI scanning electron microscope. The ZnO films prepared under the best deposition conditions found were used to fabricate a gas sensor in the desired geometry with two thick gold pads on two ends of the film to take out electrical contacts. Fig. 2 shows the schematic diagram of the experimental setup used for measuring the sensor resistivity. The ZnO sensor mounted on a Pt-heater was housed within an airtight chamber, with gas inlet and