Materials Science and Engineering C 77 (2017) 245–256

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

High performance hydrogen sensor based on Mn implanted ZnO nanowires array fabricated on ITO substrate

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A R T I C L E I N F O

Article history:
Received 22 October 2016
Received in revised form 9 December 2016
Accepted 25 March 2017
Available online 30 March 2017

Keywords:
Nano-wires
ZnO-Mn thin films
ITO substrate
Spray pyrolysis
FE-SEM
H_2 sensor

A B S T R A C T

In the present research, we propose a novel approach for the detection of hydrogen gas using Mn implanted ZnO nanowires fabricated onto ITO coated glass substrate by chemical spray pyrolysis deposition. The effect of Mn concentration on the structural, optical and morphological properties of ZnO films were investigated. X-ray diffraction studies showed that the Mn implanted ZnO films were grown as a polycrystalline hexagonal wurtzite phase without any impurities. The (101) peak position of ZnO-Mn films was shifted towards a lower angle with increasing Mn concentration. The optical band gap decreased from 3.45 eV to 3.23 eV with increasing Mn content. PL spectra, revealed sharp and strong near band edge emission which suggests that ZnO nanowires exhibit high crystalline quality. FE-SEM images of Mn implanted ZnO show perfectly aligned nanowires for all the films fabricated on ITO. The material (Zn, O, Mn) was confirmed by EDX spectra. The hydrogen sensing mechanism of the Mn implanted ZnO nanowire sensor was also discussed. It was found that H_2 response was significantly enhanced by more than one order of magnitude with increasing Mn doping concentrations. The studied ZnO-Mn films coated on ITO substrate can be used as a low cost and easy-fabrication hydrogen sensing material.

1. Introduction

Hydrogen gas has gained enormous attention due to its promising application as a clean energy carrier for use in future fuel and for replacing petrol as a pollutant, but it has many potential risks such as wide explosion concentration range (4–75%), low ignition energy (0.02 mJ), and high flame propagation velocity [1]. Lot of research is on-going to develop a new commercial hydrogen detector for monitoring the concentration of gases in the global environment, energy saving, detection and leak control of hydrogen. Smart sensing devices should be portable, faster and cheaper in comparison with analytical devices currently used and have sensitivities in the range from a few tens of part-per-million (ppm) to several hundreds of ppm. Generally, there are several basic categories for efficient and excellent gas sensing system: (i) high sensitivity and selectivity; (ii) rapid response time and fast recovery time; (iii) stability in performances; (iv) low operating temperature [2,3]. Gas sensing system based on semiconductors are attracting tremendous interest in recent years because of their widespread application in chemical and aerospace industries, petroleum extraction, rocket fuel and automobile, food control, etc. Much interest has been focused on the metal oxide semiconductor (MOS) sensors such as ZnO, WO_3, SnO_2, TiO_2 for hydrogen gas detection because of the structural simplicity, compact size and low manufacturing cost [4–6]. The sensing performance of metal oxide films depend on the mechanism by which target gas is detected on the surface of the films. The modification in electrical resistance induced by reactions between the target gases and the film surface is predominantly dependent on film grain size, porosity, impurities, stoichiometry, crystallinity and thickness of the film [7,8]. Moreover, nano-structured materials with large surface-to-volume ratio and surface-gas interaction exhibit upgraded sensing properties. Among different MOS nanostructures reported for hydrogen detection, Zinc oxide (ZnO) have drawn considerable attention due to its inherent electrical conductivity, excellent selectivity and high sensitivity [9]. During the past few years, one dimensional ZnO nanostructures (nano-rods, wires, fibers, tubes) have attracted great research interest due to their potential use as solar cells, gas sensing devices, light emitting diodes, spintronic devices and transparent thin film transistors. In addition, dopants are essential for the generation of oxygen vacancies in ZnO nanostructures and enhance the sensor response [10]. The doping of transition metal elements into ZnO offers a feasible means of fine tuning the band gap to make them suitable for gas sensors.

Until now, numerous experimental studies have been tried to grow ZnO based MOS with various transition metals such as Ni, Fe, Cr, Mn, Co etc. [11–14]. Most of the researchers paid their special attentions on the magnetism of Fe and Cr-doped ZnO systems and few literatures deal with the luminescent and morphological properties of Mn-doped ZnO with different nanostructures [15,16]. Mn ions implanted ZnO nanowires arrays have also attracted great attention in materials

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http://dx.doi.org/10.1016/j.msec.2017.03.234
0928-4931/

development towards gas sensors. It has been reported elsewhere that doping of ZnO with Mn enhanced the oxidation action of the oxide and this has been relevant to a higher density of oxygen vacancies [17]. To date, there are no reports on Mn ions implanted ZnO nanowires arrays for H_2 sensing application, especially at room temperature. Another novelty of the present work lies in the use of ITO seed layer for selective nucleation, which result in the formation of well grown grains of ZnO, favorable for sensing. Moreover, ITO coated glass substrate has many excellent properties, such as good conductivity, low resistivity, high optical transparency and high work function [18].

The sensing behavior of ZnO depends on its composition, microstructure (porosity, surface-to volume ratio) and grain size. Numerous techniques have been employed to dope metal ions into semiconductor, such as electron beam deposition [19], pulsed laser deposition [20], chemical vapor deposition [21], and magnetron sputtering [22]. In the present work, we used spray pyrolysis technique for the growth of Mn ions implanted ZnO nanowires due to the advantages of excellent control over the layer's properties. It is a convenient and simple method for large area substrate coating, effective low cost process of generating high quality stoichiometric film, high crystalline, stratified structures and potential for scale-up to achieve homogeneous incorporation. Comparatively speaking, a novel spray pyrolysis deposition route with specially designed spray nozzle was used for our film growth. Spray pyrolysis technique allows to increase dramatically the solubility and change the role of second-phase surface properties. The incorporation of second-phase can have higher porosity of nanostructured sensing matrix, superior surface area to volume ratio, more stable crystal structure, enhanced sensitivity and selectivity of sensors, and grain size [23]. Mn implanted ZnO nanowires holds high promise for outstanding hydrogen sensor applications due to their ability to operate at room-temperature, and ability to tune the gas response by controlling the defect concentration and the diameter of the ZnO nanowire.

Following this idea, Mn implanted ZnO films with different Mn concentration were grown on ITO substrate by spray pyrolysis. The aim of this work is to evaluate the effect of Mn content on the microstructure, grain growth, luminescent and optical properties, and their interplays in ZnO films were discussed in detail. The sensing performance of the Mn ions implanted ZnO nanowires were investigated for different concentrations of H_2 gas at room temperature.

2. Experimental details

2.1. Synthesis and characterization of Mn-implanted ZnO nanowire

Highly oriented $Zn_{1-x}Mn_xO$ films were grown on ITO substrate by chemical spray pyrolysis technique. The schematic diagram of the spray pyrolysis setup used for the synthesis of Mn implanted ZnO is illustrated in Fig. 1. All the reagents and solvents involved in the experiments were of analytical grade and were used without further purification. An ITO coated glass plate, 80 nm thick and 100 mm × 100 mm × 0.7 mm in dimension was used as the substrate. In the typical synthesis, 0.1 M zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$,99.9%) was used as main precursor for all films. We added 0.02 M hexamethylenetetramine ($C_6H_{12}N_4$) as a stabilizer to the solution. Mn doping was achieved by the introduction of appropriate amount of manganese acetate tetra hydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, 99.9%). To prepare ZnO-Mn samples of different molar ratios (1 wt%, 2 wt%, 3 wt% and 4 wt%), we used Mn precursor concentration of 0.01 M, 0.02 M, 0.03 M and 0.04 M, respectively. All other parameters were kept constant. A novel spray pyrolysis deposition route was adopted to achieve uniform and well adherent nanostructured films. The atomization of the precursor solution was carried out with a specially designed spray gun consisting of two concentric glass tubes, through the inner tube flows the solution and between inner and outer the air stream. The precursor spray was

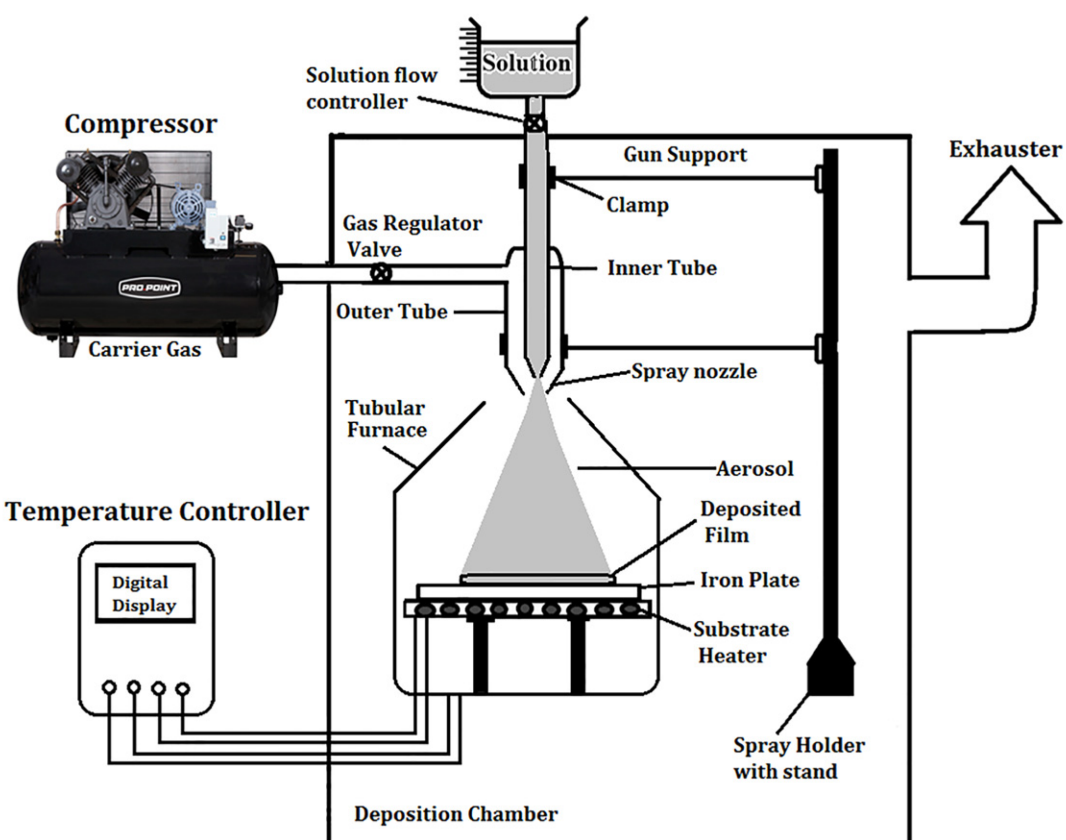

Fig. 1. Schematic of the experimental setup used for the spray pyrolysis deposition technique.