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New fabrication of zinc oxide nanostructure thin film gas sensors



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ABSTRACT

The copper doped zinc oxide thin films have been prepared by sol-gel spin coating method. The structural and morphology properties of the Cu doped films were characterized by X-ray diffraction and atomic force microscope. XRD studies confirm the chemical structure of the ZnO films. The optical spectra method were used to determined optical constants and dispersion energy parameters of Cu doped Zno thin films. The optical band gap of undoped ZnO was found to be 3.16 eV. The E_g values of the films were changed with Cu doping. The refractive index dispersion of Cu doped ZnO films obeys the single oscillator model. The dispersion energy and oscillator energy values of the ZnO films were changed with Cu doping. The Cu doped ZnO nanofiber-based NH₃ gas sensors were fabricated. The sensor response of the sensors was from 464.98 to 484.61 when the concentration of NH₃ is changed 6600-13,300 ppm. The obtained results indicate that the response of the ZnO film based ammonia gas sensors can be controlled by copper content.

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1. Introduction

Metal oxide semiconductors have been received a great attention due to their interesting electrical and optical properties for various electronic device applications [1–4]. One of metal oxide semiconductors is ZnO and it has prepared by various techniques like RF magnetron sputtering [1,2], chemical vapor deposition [3], pulsed laser deposition [4] and sol–gel process [5,6]. The sol–gel technique is one of these techniques to prepare large-area coating for technological applications [5–10].

The optical properties of the metal oxides play an important from the technological viewpoint [11]. The refractive index is an optical constant and it is related to the electronic polarizability of the

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0749-6036/\$ - see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.spmi.2013.11.009 materials. For optic devices applications, the refractive indices is important parameter. This parameter can be related to porosity in the metal oxide semiconductors. The porosity properties of any material are important for its gas sensing properties. Ammonia (NH_3) is a colorless gas with a distinctive odor. For the detection of gaseous NH_3 , the potentiometric electrodes have been used [12].

The fabrication of new ammonia gas sensors is important to detect various concentrations, because this gas has been used in various applications such as fire power plants, food processing, chemical technology, medical diagnosis, fertilizers, and environmental protection. The metal oxide semiconductors such as ZnO, SnO₂, Cr₂O₃, TiO₂ and WO₃ have been used in fabrication of the ammonia gas sensors [13–19].

In present study, nanostructure ZnO based gas sensors can be prepared and their gas response properties can be improved by controlling of nanosize and nanostructure. With this aim, we have prepared the nanostructure Cu doped ZnO films by sol gel method to fabricate ammonia gas sensors and improve the gas response characteristics. The optical and structural properties of Cu doped ZnO films were investigated using various methods. The gas sensing characteristics of the Cu doped ZnO films based gas sensors were investigated by current-time method.

2. Experimental details

The copper doped ZnO films were prepared using the precursors: zinc acetate dihydrate $[Zn(CH_{3-})]$ CO₂)₂·2H₂O;ZnAc], 2-methoxethanol and monoethanolamine (MEA). The ZnO films were doped with the various atomic ratios of 0.1 at.%, 0.5 at.%, 1 at.%, 2 at.% and 5 at.% copper contents. Firstly, the solutions were prepared for various Cu contents and were stirred at 60 °C for 2 h. After the cleaning procedure of the glass substrates in methanol, acetone and deionized water baths, the substrates were coated using the prepared solutions at 2000 rpm for 30 s using a spin coater. After the 5 times coating procedure, the films were preheated at 150 °C for 10 min in a furnace to evaporate the solvent and remove organic residuals and the solid films were obtained and the films were annealed at 400 °C for 1 h. The optical spectral curves such as diffuse reflectance, transmittance, and absorbance were measured using an integrating sphere for the SHIMADZU UV-VIS-NIR 3600 spectrophotometer. Barium sulfonate BaSO₄ was used as reference to provide a nominal 100% reflectance measurement. X-ray diffraction patterns of the films were performed using a Bruker X-ray diffractometer. The gas sensors were prepared using interdigitated contact mask with 50 µm wide and 100 µm. The schematic diagram of the cu doped ZnO film/glass substrate sensors is given in Fig. 1. The sensors characteristics were performed computerized gas sensor system. The gas concentrations of NH₃ gas were controlled using digital gas flow meters.

3. Results and discussion

3.1. Structural properties of the Cu doped ZnO films

Fig. 2 shows the AFM images of Cu doped ZnO films. The undoped and Cu doped ZnO films are formed from fibers. The particle sizes of the films were determined using a PARK system XEI software



Fig. 1. Schematic diagram of the Cu doped ZnO film/glass substrate sensors.

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