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Effect of nickel doping on structural, optical, electrical and ethanol sensing properties of spray deposited nanostructured ZnO thin films

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Abstract

Undoped and nickel (Ni)-doped ZnO thin films were spray deposited on glass substrates at 523 K using 0.1 M of zinc acetate dihydrate and 0.002–0.01 M of nickel acetate tetrahydrate precursor solutions and subsequently annealed at 723 K. The effect of Ni doping in the structural, morphological, optical and electrical properties of nanostructured ZnO thin film was investigated using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), UV–vis Spectrophotometer and an Electrometer respectively. XRD patterns confirmed the polycrystalline nature of ZnO thin film with hexagonal wurtzite crystal structure and highly oriented along (002) plane. The crystallite size was found to be increased in the range of 15–31 nm as dopant concentration increased. The SEM image revealed the uniformly distributed compact spherical grains and denser in the case of doped ZnO thin films. All the films were highly transparent with average transmittance of 76%. The measured optical band gap was found to be varied from 3.21 to 3.09 eV. The influence of Ni doping in the room temperature ethanol sensing characteristics has also been reported.

Keywords: A. Films; C. Electrical properties; D. ZnO; E. Sensors

1. Introduction

In the recent past, detection and control of volatile organic compounds (VOCs) in atmosphere emitted by textile, paint, pesticide, medical, fragrance and food processing industries has been a major concern for scientists and engineers [1–4]. The presence of such toxic and carcinogenic VOCs in environment will have severe health impacts and lead to premature death. In this scenario, one of the most versatile VOCs namely ethanol being a low cost alternative fuel and industrial solvent has posed a major threat to the environment. Discharging of excess concentration of ethanol in atmosphere may create skin and eyes irritation, nausea and vomiting, central nervous system depression and acidosis [4]. Hence, to detect and control the ethanol concentration in environment has emerged as a new challenge to avoid such health risks. In this context, metal oxide gas or VOC sensors will have to play a prominent role to detect ethanol in the atmosphere [1]. Among the various metal oxide materials, zinc oxide (ZnO) has attracted many scientists and engineers because of its versatile and tunable nature [5,6].

ZnO thin film with different nanostructured morphology is a fascinating platform to achieve desirable structural, morphological, electrical, electronic, optical, magnetic and optoelectronic properties [7]. In addition to its inherent properties like wide band gap (3.37 eV), large exciton energy (60 meV), better thermal and chemical stability, transparent conducting nature, etc., its adaptability towards metal ion doping has widened its applications in the fields of thin film transistor, solar cell, gas sensors, ultraviolet light emitting diodes, lasers, field emitters, piezoelectric devices, photo detectors, flat screen displays, sun screens, spintronics, etc. [6]. Doping ZnO with different kinds of anions or cations is one of the best ways to modulate or change the morphology, carrier concentrations, density of states, transmittance, band gap, electrical

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conductivity, magnetic properties, etc. [8]. Especially doping with transition metal ions has a profound effect on the materials characteristics. In the recent past, researchers have doped ZnO with Cr [9], Mn [10], Fe [11], Co [12], Ni [13], Cu [14] and observed variations across all types of physical properties and noticeably with transport properties. In particular Ni-doped ZnO thin films have been synthesized by various deposition techniques such as spin coating [15], sol–gel [16], spray pyrolysis [17], colloidal [18], sputtering [19], pulsed laser deposition [20], metal organic chemical vapor deposition [21], etc. Among them, spray pyrolysis technique has many advantages like simplicity, cost effectiveness, large scale production using low cost raw materials, etc. [22]. Further, optimization of spray deposition parameters like precursor concentration (both host and dopants), precursor medium, solution flow rate, substrate–nozzle distance, carrier gas, carrier gas pressure, substrate temperature, spray time, pH can be achieved to obtain the desired morphology, transport and sensing properties. Since, reports on the influence of variations of molar concentrations of Ni doping in ZnO thin films synthesized by spray pyrolysis technique as well as on the effect of Ni doping on the ethanol sensing characteristics are very few, we report the synthesis and characterization of undoped ZnO and Ni-doped ZnO thin films with varying molar concentrations obtained by optimizing the aforesaid spray deposition parameters.

2. Materials and methods

2.1. Film deposition

Undoped and various concentrations of Ni-doped ZnO films were deposited on glass substrates by fully automated spray pyrolysis deposition technique (HOLMARC HO-TH-O4, India). The glass slides (Blue Star, Mumbai) were washed systematically with acetone, 2-propanol and deionized water (Millipore, USA) using Ultrasonic Bath (Supersonics, Mumbai) and dried in hot air oven at 323 K for 30 min in order to remove the organic matters and other moistures present in the environment. The cleaned glass substrates were carefully

Table 1
Optimized deposition parameters.

Parameters	Values
ZnO precursor	Zinc acetate dehydrate (S1 = 1.098 g)
Ni dopant precursor	Nickel acetate tetrahydrate (S2 = 0.025 g, S3 = 0.050 g, S4 = 0.075 g, S5 = 0.010 g, S6 = 0.012 g)
Substrate temperature	523 K
Solvent	Deionized water (50 ml)
Carrier gas pressure	2.5 mbar
Solution flow rate	2 ml min^{-1}
Distance between nozzle and substrate	15 cm
Spray area	15 cm min^{-1}
Spray angle	90°
Spray nozzle diameter	0.2 mm
Post annealing temperature	723 K

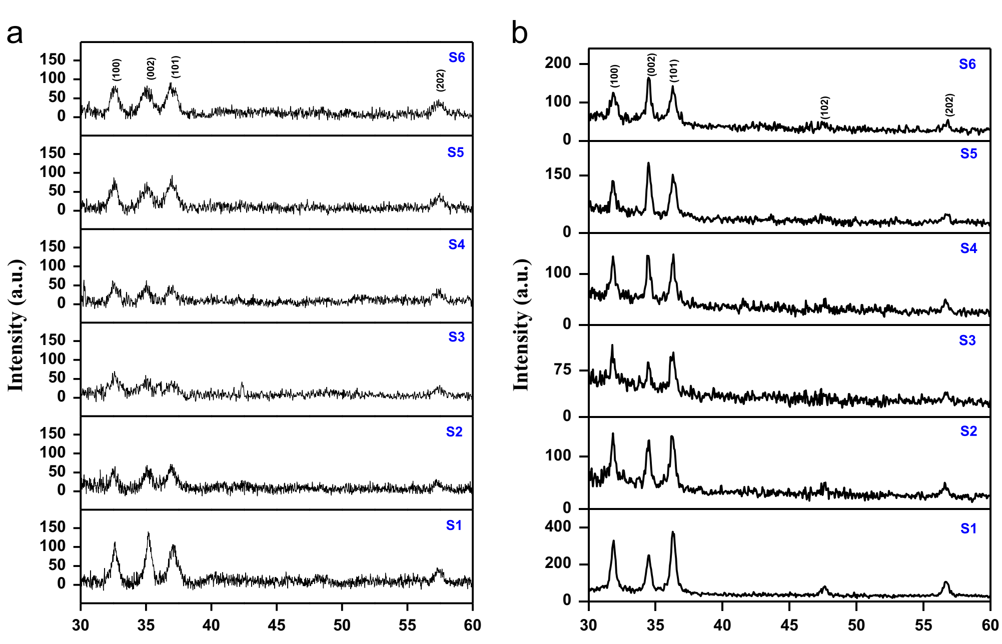

Fig. 1. XRD patterns of (a) as-deposited and (b) annealed undoped and Ni doped ZnO thin films.