Journal of Colloid and Interface Science 466 (2016) 352–359

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

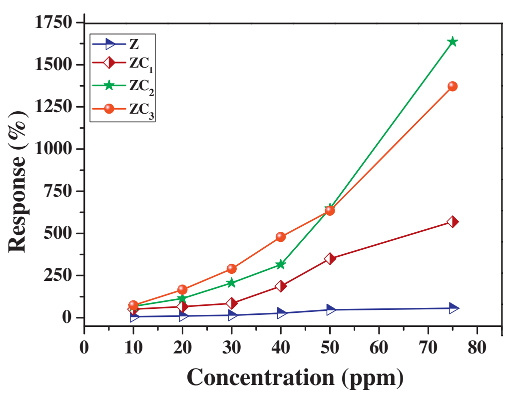
journal homepage: www.elsevier.com/locate/jcis

# Ambient temperature operated acetaldehyde vapour detection of spray deposited cobalt doped zinc oxide thin film

S. Shalini, D. Balamurugan *

*Functional Nanomaterials Lab, Centre of Nanotechnology & Advanced Biomaterials (CeNTAB) and School of Electrical & Electronics Engineering, SASTRA University, Thanjavur 613 401, Tamil Nadu, India*

## GRAPHICAL ABSTRACT




ARTICLE INFO

*Article history:*
Received 6 September 2015
Revised 19 December 2015
Accepted 22 December 2015
Available online 23 December 2015

*Keywords:*
ZnO
Thin film
Nanostructure
Spray pyrolysis
Chemiresistive
Acetaldehyde

ABSTRACT

Undoped and Co-doped ZnO thin films were prepared by a home built spray pyrolysis method. X-ray diffraction results indicate that both undoped and Co-doped ZnO have a polycrystalline nature and a preferential orientation peak in the (002) plane. From a field-emission scanning electron micrographs of annealed films, a uniform distribution of nanoparticles along with nanorods was observed. UV–Visible measurement indicated that all the films are transparent in the visible region. The electrical resistance was also reported. The acetaldehyde sensing behaviour of the prepared undoped and Co-doped ZnO thin films was studied using the chemi-resistive method at ambient temperature (~30 °C). In the presence of 10 ppm of acetaldehyde vapour, the Co-doped ZnO thin films showed good sensing response of 74% with fast response and recovery time of 3 s and 110 s respectively.



## 1. Introduction

Acetaldehyde is one of the most important compounds in the aldehydes group, occurring widely in nature and produced at large scale in industry. It is used as an aromatic agent and is found naturally in fruits and fruit juices. Occurring naturally during fermentation, it is found at low levels in certain foodstuffs. Acetaldehyde vapour is colourless and has a pungent odour. It is also an intermediate product for the production of other chemicals (e.g. Acetic acid). Acetaldehyde is extremely irritating to humans at higher concentrations (greater than 50 ppm) and it is a probable carcinogen, with other possible side effects of overexposure including coughing, pulmonary edema, erythema (redness of skin) and

* Corresponding author.
*E-mail address:* balamurugan@eee.sastra.edu (D. Balamurugan).

http://dx.doi.org/10.1016/j.jcis.2015.12.044
0021-9797/

necrosis [1]. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned a threshold limit for acetaldehyde exposure of 100 ppm (180 mg/$m^3$) as a total weight average (TWA) for a normal eight hour workday and a forty hour work week, with a short term exposure limit (STEL) of 150 ppm (270 mg/$m^3$) for periods not to exceed 15 min. Since its boiling point at atmospheric pressure is 20.2 °C, it is an extremely volatile liquid. Meanwhile, OSHA has set the dangerous exposure limit for acetaldehyde at 25 ppm in eight hours [2].

Acetaldehyde can occur both indoors and outdoors. The main indoor sources of acetaldehyde vapour include matte emulsion paints, wood varnish, linoleum, laminate, cork/pine flooring, wooden ceiling and so on [3]. Outdoor sources include incomplete wood combustion, coffee roasting, burning of tobacco, vehicle exhaust fumes and waste processing, cement kilns and automotive and diesel exhaust. Acetaldehyde can also generate ethanol from the liver, finally degrading to carbon dioxide and water through acetic acid. It also plays a major role in the wine making process [4].

Zinc oxide (ZnO) has a wide band gap (3.37 eV) and high exciton binding energy (~60 meV) [5]. ZnO is an important material for optoelectronic devices to be used in the blue and violet region because of its wide band gap [6]. ZnO nanoparticles include different morphologies such as nanowire, nanobelt, nanorod, nanosphere and nanoflowers [7]. ZnO thin films have been used in a variety of applications, including light emitting diodes [8], antireflective coatings [9], heat mirrors [10], surface acoustic wave devices [11], Schottky diodes [12], spin electronics [13], photo detectors [14] and gas sensors [15]. ZnO thin films can be prepared using various techniques, including ultrasonic spray [16], DC magnetron sputtering [17], spin coating [18], the sol–gel method [19], electrodeposition method [20], electrostatic spray deposition method [21] and spray pyrolysis method [22]. In our present work, we chose the spray pyrolysis method for depositing the film because of its low cost, the large deposition area covered, easy to handle, the lack need for high vacuum during deposition process and to obtain different morphological structures by changing the spray parameters.

Li et al. [23] reported ethanol and CO sensing properties of Co-doped ZnO thin films prepared by the electrodeposition method at 90 °C. Ganbavle et al. [24] reported LPG gas sensing studies at low temperature with nanocrystalline Co-doped ZnO thin films deposited by the spray pyrolysis method and sensitized with a Pd catalyst. Rambu et al. [25] reported the methane detection properties of Co-doped ZnO thin films prepared by the spin coating method. Liu et al. [26] reported the acetone detection properties at different operating temperatures of Co-doped ZnO thin films deposited by the electro spinning method. Giberti et al. [11] reported the high sensitivity of acetaldehyde detection of a single and mixed metal oxide nanostructured material. Benramache et al. [16] reported the structural, optical and conductivity properties of Co-doped ZnO thin film deposited by spray pyrolysis method. In the present work, we report acetaldehyde vapour sensing studies at ambient temperature (~30 °C), along with structural, morphological, optical and electrical studies of undoped and Co-doped ZnO thin films.

## 2. Materials and methods

### 2.1. Thin film deposition

The undoped and cobalt (Co) doped ZnO thin films were prepared by the home-built spray pyrolysis method [27]. 0.05 M of zinc acetate dihydrate (Zn $(CH_3COO)_2{\cdot}2H_2O$, Sigma Aldrich, purity 99.99%) was taken as the primary precursor salt and dissolved in 50 mL of deionized water. The dopant precursors of cobalt acetate tetra hydrate (Co $(CH_3COO)_2{\cdot}4H_2O$, Loba Chemie, Purity 98.5%) with different concentrations (typically 0.1 mM, 0.2 mM and 0.3 mM) were dissolved in 50 mL of deionized water and mixed with the prepared ZnO precursor solution. Initially, glass substrates were cleaned with deionized water and then placed on a hot plate. The substrate deposition temperature and angle of the spray gun were maintained at 250 °C and 45°. Compressed dry air acts as a carrier gas in order to transform the precursor solution into a fine mist, typically kept at 2 kg/$cm^2$. The solution flow rate was maintained at 3 mL/min. The spray time and interval between successive sprays was maintained at 5 s and 75 s, respectively. After deposition, all the films were annealed at 300 °C for 3 h using a muffle furnace and labelled as Z (Undoped ZnO), $ZC_1$ (1 wt% Co), $ZC_2$ (2 wt% Co) and $ZC_3$ (3 wt% Co). The pyrolytic reaction of zinc acetate to zinc oxide (ZnO) is given below [28].

$$4Zn(CH_3COO)_{z(s)} \rightarrow 4Zn(CH_3COO)_{2(g)} + H_2O_{(aq)} \rightarrow Zn_4O(CH_3COO)_{(g)} + 2CH_3COOH \quad (1)$$

$$Zn_4O(CH_3COO)_{(g)} + 3H_2O \rightarrow 4ZnO_{(s)} + 6CH_3COOH_{(g)} \quad (2)$$

### 2.2. Characterisation

Structural studies were determined by X-ray diffractometer (XRD, D8 Focus, Bruker, Germany), with Cu K$\alpha_1$ radiation ($\alpha$ = 1.5406 Å) operating at 40 kV with a scanning range of 30° and 70°. The surface morphology of the deposited films was examined by field-emission scanning electron microscope (FE-SEM, JEOL-6701 F, Japan). Elemental compositions were confirmed with Energy Dispersive X-ray Spectroscopy (EDS). Optical studies were carried out using a UV–Visible spectrometer (Perkin Elmer Lambda 25) and the electrical conductivities of the films were determined by the Hall Effect measurement system (ECOPIA-HMS-3000 VER 3.51.5).

### 2.3. Sensing measurement

The gas sensing properties of the undoped and Co-doped ZnO thin films towards acetaldehyde vapour were studied using a home-built testing chamber of 1.5 L capacity and with a septum provision to inject the target liquid into chamber through a chromatographic syringe and venting through a vacuum pump.

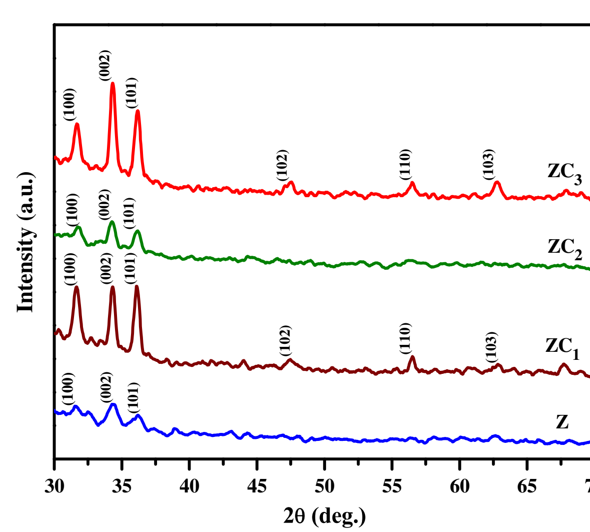



**Fig. 1.** X-ray diffraction pattern of undoped ZnO (Z) and Co-doped ZnO ($ZC_1$, $ZC_2$ and $ZC_3$).