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Acetone vapour sensing characteristics of cobalt-doped SnO_2 thin films

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Abstract

Gas sensing behaviour of cobalt-doped tin oxide (Co–SnO_2) thin films, synthesized by conventional spray pyrolysis technique, has been investigated for carbon dioxide, oxygen and acetone vapour. Structural and elemental analysis of the Co–SnO_2 films was carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDAX). The XRD spectrum revealed the polycrystalline nature of the film with a mixed phase comprising of SnO_2 and Co_3O_4. The surface morphology, as seen in the SEM image, was observed to be granular, uniformly covering the entire substrate surface. The gas/vapour sensing studies performed in dry air at different temperatures in the range of 50–300 °C indicated better sensing characteristics for acetone vapour as compared to carbon dioxide and oxygen gases. The influence of cobalt concentration and operating temperature on the sensor performance has also been investigated.

Keywords: Gas sensor; Spray pyrolysis; Acetone vapour; SnO_2; Co_3O_4

1. Introduction

Over a period of three decades, metal oxide semiconductor based sensors have been under extensive investigations due to their applications in industrial and domestic sectors [1–3]. Amongst the large number of metal oxides, particularly SnO_2, ZnO, WO_3 and TiO_2 have been the materials of choice in most of these investigations. It has been widely accepted that the gas sensing mechanism consists of 'receptor' and 'transducer' functions. The receptor function deals with the surface chemical/catalytic property, whereas the transducer function is due to the surface semiconducting property and grain size of the base oxide used. The receptor function can be tailored by dispersing foreign species on the metal oxide grains. In this regards, attempts have been carried out by 'doping' the base metal oxide systems with metallic species, such as Al, Cu, Pt, Pd, etc., in order to obtain better sensor characteristics in terms of sensitivity, selectivity and response time [4–7].

The recent advances in synthesis of nanostructures having different shapes and sizes have been exploited to design and fabricate smart sensors, thereby tailoring the transducer function responsible for the sensing mechanism [8–10]. However, the complexity involved in the synthesis process and need of advanced characterization techniques limit the applicability of the nanomaterial based sensor systems. In this context, the simple and cost effective conventional synthesis techniques, such as vacuum evaporation, sputtering, chemical bath deposition, spray pyrolysis, etc., used for making thin film sensors are still attractive.

In addition to the sensing of oxidizing and reducing gases, various researchers have attempted detection of volatile organic compounds (VOCs) [11–13]. In this regard, Patel et al. have reported sensing characteristics of an indium tin oxide thin film for methanol vapour [11]. Fabrication of a SnO_2 based sensor array for recognition of VOCs has been attempted by Lee et al. [12]. The authors have studied the effect of various additives such as Pd, Pt, La_2O_3, CuO, Sc_2O_3, TiO_2, WO_3, ZnO and V_2O_5 on the sensitivity and the selectivity of the SnO_2 sensor array. The authors have observed high and selective sensitivity to the VOCs at 400 °C. Cobalt oxide Co_3O_4, owing to its better catalytic activity, can be thought to be an active additive in the base oxide matrix so as to improve its sensing performance. In this regard, a Co_3O_4 based isobutene sensor operating at low temperature has been reported by Choi and Min [8]. Very recently, Cantalini et al. have studied sensing behaviour of sol–gel derived composites of SnO_2 and Co_3O_4 for reducing gases, such as H_2

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and CO [10]. The observed better sensing properties have been attributed to the active role played by Co_3O_4 grains and porosity in the film. The Co_3O_4 grains combine with SnO_2 electronically by forming p–n junctions, resulting in an increase in electrical resistance of the device. Upon exposure to the gas environment, reduction of Co_3O_4 molecules results in destruction of the p–n junctions, there by exhibiting sensing action.

In this paper we report the sensing characteristics of cobalt-doped tin oxide (Co–SnO_2) thin films for carbon dioxide, oxygen and acetone vapour. The Co–SnO_2 thin films were synthesized on glass substrates using spray pyrolysis method and were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The elemental composition was determined by employing an energy dispersive X-ray spectrometer (EDAX). The sensing behaviour was studied at different temperatures in the range of 100–300 °C. Influence of the cobalt concentration on the sensor performance has also been studied. The Co–SnO_2 films show better sensor performance to acetone vapour as compared to carbon dioxide and oxygen. The sensing characteristics are found dependent on the cobalt concentration and operating temperature.

2. Experimental

The Co–SnO_2 thin films were synthesized on glass substrates by employing an indigenously designed and fabricated spray pyrolysis system. The precursor solution was prepared by dissolving 1.5 g powder of stannic chloride ($SnCl_4{:}5H_2O$) and 0.125, 0.25, 0.50, 0.75, 1.0 and 1.25 g powder of cobalt acetate ($(CH_3COO)_2Co{:}4H_2O$) separately in 10 ml solvent (a mixture of de-ionized water and methanol in a volume ratio of 1:4). The different amounts of cobalt acetate powder correspond to 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M solutions. The glass substrates were cleaned using a chromic acid solution, followed by rinsing with double distilled water. The substrates were heated to ∼400 °C and 5 ml of the precursor solution (4 ml of the stannic chloride solution and 1 ml of a cobalt acetate solution) was sprayed over the hot substrates using compressed air as a carrier gas. The spray rate was monitored at ∼2 ml min^{-1}. The thin films synthesized by spraying the 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M solutions are hereafter termed as S0.05M, S0.15M, S0.2M, S0.3M, S0.4M and S0.5M.

The structural and morphological characterizations of the Co–SnO_2 thin films were performed on an X-ray diffractometer (D-8 Advance Brucker, Germany) and a scanning electron microscope (JEOL JSM-6360), respectively. The SEM images were recorded with an accelerating voltage ∼20 kV and a filament current ∼60 mA.

The sensing characteristics measurements were carried out under controlled ambiences of the test gas/vapour in a specially designed bell jar (volume 3 l). The schematic of the experimental setup is shown in Fig. 1. The bell jar was mounted onto a base plate equipped with electrical feedthroughs and a gas inlet port. The sensor element (a 15 mm × 20 mm glass plate with a spray deposited film) was mounted on a resistive heater, which facilitated variation in film temperature. A tiny chromel–alumel thermocouple was used to measure the film temperature, which

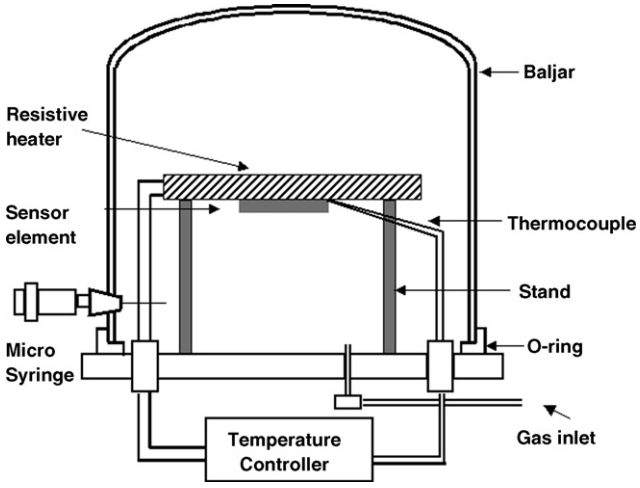

Fig. 1. Schematic of the gas/vapour sensing system.

was monitored by a temperature controller. The thin film resistance was measured using a two-probe method, by putting two ohmic contacts (separation ∼1 cm) on the film surface using conducting silver paste. After mounting the sensor element and making all electrical connections, the bell jar was evacuated to rough vacuum using a rotary pump and dry air was admitted in it. The sensing characteristics were measured under a controlled test gas/vapour ambience, created by introducing a known quantity of it into the bell jar. A fixed quantity of acetone was injected into the jar through a side port using a micro-syringe, while gases such as carbon dioxide and oxygen were introduced through an inlet mounted onto the base plate. Enough time was given for temperature stabilization, before introducing the test gas/vapour.

The sensing performance of a Co–SnO_2 thin film was tested for oxygen, carbon dioxide and acetone vapour. The concentration of acetone vapour was varied by injecting 0.02, 0.04, 0.06, 0.08, 0.1, 0.12 and 0.14 ml of acetone in the bell jar through a microsyringe. The sensing characteristics were investigated at least for three samples synthesized under identical experimental conditions.

3. Results and discussion

The X-ray diffraction spectra of the Co–SnO_2 thin films, corresponding to 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M cobalt acetate molarities, synthesized at 400 °C show well defined diffraction peaks, indicating formation of polycrystalline phases. A typical X-ray diffraction spectrum of the S0.2M film (0.2 M cobalt acetate) is depicted in Fig. 2. The XRD spectrum is identical to that reported by various researchers [4,5]. The diffraction peak indexing, done by comparing the observed d values to the standard data base (JCPD: 21–1250), clearly revealed formation of the SnO_2 phase with tetragonal structure. A low intense diffraction peak corresponding to Co_3O_4 is also observed in the spectrum. In the present studies, the intensity of the Co_3O_4 diffraction peak was found to be nearly the same in all the XRD spectra of films synthesized using different cobalt acetate molarity solutions.