Journal of Alloys and Compounds 657 (2016) 414–421

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Development of $CoFe_2O_4$ thin films for nitrogen dioxide sensing at moderate operating temperature

A.A. Bagade, K.Y. Rajpure*

Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India

ARTICLE INFO

Article history:
Received 24 July 2015
Received in revised form
5 October 2015
Accepted 13 October 2015
Available online 19 October 2015

Keywords:
Spray pyrolysis
Cobalt ferrite
XRD
FESEM
Dielectric properties
Gas sensing

ABSTRACT

Cobalt ferrite thin films were deposited onto quartz substrates by spray pyrolysis technique and their gas sensing properties were investigated. X-ray diffraction study confirms that films are polycrystalline in nature and exhibit single phase spinel cubic crystal structure. DC electrical resistivity measurement indicates the semiconducting nature of the films. The surface morphology study confirms the formation of grains structure with grain size about 200–400 nm. Room temperature variation of dielectric properties with frequency suggests the normal dielectric performance of the cobalt ferrite thin film. The influence of quantities of spraying solutions on the operating temperature, sensitivity and selectivity, gas concentrations, response and recovery characteristics of gas sensor are systematically tested. The maximum gas response 95% was observed for film prepared at 50 mL quantity of solution for 80 ppm NO_2. The films are extremely selective towards NO_2 as compared to other target gases. Gas response attains nearly 90% of its initial value after 90 days indicates good durability of the films.

1. Introduction

Spinel structured ferrites are imperative scientific materials as they possess both semiconductor and magnetic properties [1]. Spinel ferrite materials have attracted the research interest due to their practical applications in many research fields [2–4]. The spinel ferrites having a chemical composition $M^{2+}Fe_2O_4$ (M = Cu, Mn, Mg, Co, Zn, Ni, Cd, etc.) are widely used as magnetic materials.

Recently, some spinel ferrite thin films have been studied in the gas sensor application as they show high sensitivity and selectivity to certain gases present in the atmosphere [5]. The general gas sensing mechanism is based on the chemisorptions of oxygen on the surface of gas sensing material, followed by charge transfer during the reaction between oxygen with gas molecules. Therefore, its resistance changes during and after the expose of the gas on the surface of metal oxide semiconductor [6]. The spinel ferrite in which the divalent transition metal ion i.e. M^{2+} was incorporated into the lattice of the parent structure was established to be a promising material in detecting of the gases presence of the atmosphere [7]. From the gas sensor application point of view low density and high surface area is required because they show good sensitivity and stability for detection of various gases [8]. The gas response of the sensor depends on the morphology, annealing temperature, ferrite composition, concentration and which type of target gas to be used for detection [9]. Cobalt ferrite thin films have been used in industrial applications because they have strong anisotropy, good mechanical hardness and chemical stability [10,11]. Lee et al. [12] synthesized the cobalt ferrite thin films by sol–gel technique and studied the structural and magnetic properties. They reported that the $CoFe_2O_4$ film prepared by sol–gel technique could be used for high-density recording media if the grain size is 10 nm while maintaining its magnetic property. The spinel cobalt ferrite thin films have extensively used in research because of their applications in frequency device [13,14]. Pulsed laser deposition (PLD) [15], RF magnetron sputtering [16], Sol–gel method [17], spray pyrolysis [18], electron beam evaporation [19] etc. have been used to prepare ferrite thin films. Amongst the various techniques, spray pyrolysis is one of the best techniques as it is simple, cost-effective and useful for preparation of ferrite thin films [20]. Tudorache et al. [21] prepared $NiCoFe_2O_4$ thin films by spin coating technique for gas sensing application. The highest sensitivity for ethyl alcohol vapors was observed for low cobalt contents and higher response was observed for acetone at large cobalt contains thin films. Xiangfeng et al. [22] reported nanocrystalline $CoFe_2O_4$ by hydrothermal method for ethanol gas sensor and investigated their gas sensing properties. They found that the

* Corresponding author.
E-mail address: rajpure@yahoo.com (K.Y. Rajpure).

http://dx.doi.org/10.1016/j.jallcom.2015.10.115

$CoFe_2O_4$ nano crystals are used for detecting very low concentration of triethylamine and ethanol gases. Sutka et al. [23] prepared n-type $ZnFe_2O_4$ thin films by spray pyrolysis technique for gas sensor application and they obtain fast response time for ethanol gas at 1 ppm concentration. The similar type of other spinel oxide semiconductor (MFe_2O_4) shows gas sensor response to NO_2 at various experimental conditions. Zhuiykov et al. [24] investigated NO_2 sensing properties over the temperature range 600–700 °C of the zinc ferrite. They observed maximum gas response at 436 ppm at 700 °C operating temperature. The gas response also increases with increase in NO_2 concentration. Darshane and Mulla [25] reported the gas sensor performance towards NO_x of magnesium ferrite nano-particles by using a simple molten salt method. They found that 52% gas response for 1% Pd doping then decreases further increasing in Pd doping. Zhang et al. [26] prepared $ZnCo_2O_4$ nanotube by using a template assisted method and their gas sensing properties towards various gases was studied. The $ZnCo_2O_4$ nanotube shows maximum 1.72 gas response for 400 ppm NO_2 at 300 °C operating temperature. Niu et al. [27] synthesized zinc ferrite by micro-emulsion method and studied their gas sensing properties. The maximum gas response S = 2.4 was observed for $ZnFe_2O_4$ for 50 ppm NO_2 at 270 °C operating temperature.

We have already reported [20] physicochemical properties of spray deposited $CoFe_2O_4$ thin films. The substrate temperature was optimized to be 400 °C. In continuation of this work, in this paper effect of the quantity of spraying solution on $CoFe_2O_4$ thin films is discussed. Further their NO_2 gas sensing properties are studied.

2. Experimental

2.1. Synthesis of $CoFe_2O_4$ thin films

The cobalt ferrite thin films were deposited onto the preheated quartz substrates using simple chemical spray pyrolysis technique [20]. The spraying solution was sprayed onto preheated quartz substrates at different quantities of spraying solutions an interval of 10 mL. The as-deposited cobalt ferrite thin films were annealed at the 900 °C for 4 h in ambient atmosphere at 2°/min constant heating rate. These annealed ferrite thin films were characterized for their physicochemical as well as gas sensing properties.

2.2. Characterization techniques

To analyze the crystalline quality and phase identification of annealed $CoFe_2O_4$ thin films, XRD studies were carried out using Bruker D2-Phaser X-ray powder diffractometer with Cu-Kα (λ = 1.5406 Å) radiation recorded in ranges of 20–80°. The thickness of the annealed films was measured by using AMBIOS, USA XP-I surface profiler and scanning electron microscopy. The DC electrical resistivity of ferrite thin films was measured by using the two probe method with a high sensitivity Keithley electrometer model-6514. The surface morphology of the films was investigated using a Mira-3, Tescan, Brno-Czech Republic, Field emission scanning electron microscope (FE-SEM). The dielectric measurements of the cobalt ferrite thin films were carried out using a high precision LCR meter bridge (HP-6284A) in the frequency range 20 Hz to 1 MHz at room temperature.

2.3. Gas sensing measurements

For gas sensing measurements the silver contacts were made into the $CoFe_2O_4$ thin film, which were placed in a specially designed stainless steel chamber having diameter 7 cm and height 15 cm. The operating temperature was varied, ranging from 150 °C to 250 °C. The NO_2 gas was injected into the gas chamber with a calibrated syringe. The Cromel–Alumel thermocouple was used to measure the operating temperature and connected to the heating system. The gas response of the films in both air and in presence of the gas was measured at various gas concentrations at constant operating temperature 150 °C. Gas sensing measurements were carried out at locally fabricated gas sensing unit equipped with gas flow meters and change in resistance was measured on the Keithley electrometer (6514). The gas response was calculated by using the relation [28].

$$\text{Gas response } (\%) = \frac{R_{air} - R_{gas}}{R_{air}} \times 100 \quad (1)$$

where, R_{air} is the resistance in the air and R_{gas} is the resistance in the presence of the gas. Response and recovery times mean the time for the sensor to reach 90% of the final resistance value during gas exposure and at the end of gas exposure, respectively.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1 shows X-ray diffraction (XRD) patterns of the annealed $CoFe_2O_4$ thin films deposited at various quantities of the spraying solution. A matching of inter planar spacing values (d) of $CoFe_2O_4$ using JCPDS card No-02-1045 confirms the spinel cubic crystal structure. It is observed that, as the quantity of the spraying solution increases the crystallinity of films increases up to 50 ml and then decreases. The lower intensity peaks are observed in $CoFe_2O_4$ films due to the lower film thickness. The crystallite size is calculated by using the Scherrer's formula [29]. The crystallite size of the films varies with varying quantities of the spraying solution. In the present study, the thickness of the films increases with increase in quantities of the spraying solutions. Crystallite size becomes larger in the thinnest films and is directly correlated to the film thickness. Similar variation of the crystallite size as a function of film thickness is reported by Bouderbala et al. [30]. The exact value of the lattice parameter has been calculated by plotting the graph of Nelson Riley function (NRF) versus the lattice parameter for every plane. The NRF is a function of the Bragg angle θ calculated using

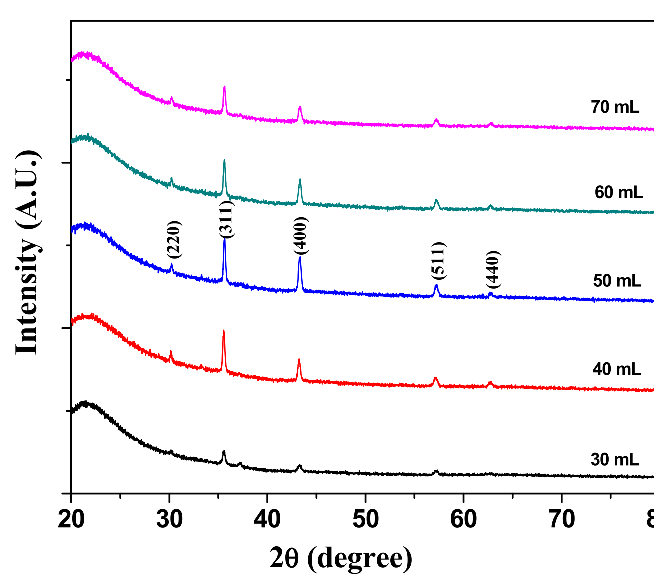

Fig. 1. X-ray diffraction patterns of annealed $CoFe_2O_4$ thin films deposited at various quantities of spraying solutions.