Sensors and Actuators B 261 (2018) 522–530

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Ethanol sensing properties of sprayed β-In_2S_3 thin films

R. Souissi [a], N. Bouguila [b], A. Labidi [a,*]

[a] Université de Carthage, Laboratoire des Matériaux, Molécules et Applications IPEST, BP 51, La Marsa 2070, Tunis, Tunisia
[b] Laboratoire de Physique des Matériaux et des Nanomatériaux appliqué à l'environnement, Faculté des Sciences de Gabès, Université de Gabès, Cité Erriadh, Zrig, 6072 Gabès, Tunisia

ARTICLE INFO

Article history:
Received 27 June 2017
Received in revised form 14 December 2017
Accepted 22 January 2018

Keywords:
In_2S_3 thin films
Spray pyrolysis
Adsorbed oxygen
Ethanol sensing

ABSTRACT

This work reports on the integration of In_2S_3 material for use as an alcohol sensor. In_2S_3 thin films were deposited on glass substrates by spray pyrolysis technique. The morphology and microstructure of the obtained samples were characterized by XRD, SEM, TEM and EDX methods. The response to ethanol vapor at different concentrations was measured in the range of operating temperatures 250 °C–400 °C using DC electrical characterization. The In_2S_3 based sensor showed good sensitivity towards ethanol at optimal working temperature of 350 °C. The sensing mechanism of In_2S_3 semiconductor was developed on the bases of the reaction between the reducing ethanol vapors with the chemisorbed oxygen. The sensor rapidity, selectivity, stability and reproducibility were also studied.

1. Introduction

Gas sensors are commonly used in medical, environmental, and domestic applications for detecting toxic and combustible gases [1,2]. Metal oxides like ZnO, SnO_2, WO_3, Fe_2O_3, In_2O_3... are often favorite for gas sensing owing to their thermal stability, good response and reversibility [3,4]. In addition, to enhance sensitivity and to get lower operating temperatures, noble metals are eventually added [5,6]. However, these types of sensors still suffer from such troubles as a long-term stability and a high-working temperature. The progress of solid state gas sensors was the entity of several researches in the world. In this context, we can quote the example of In_2S_3. Few studies have been devoted to the gas-sensing properties of the indium sulphide In_2S_3. Nevertheless, In_2S_3 has been extensively used for optoelectronic applications such as solar energy conversion [7], photo detector [8], photo electrochemical cells [9] and hetero-junction In_2S_3/polymeric [10].

Generally, as grown In_2S_3 film is N-type semiconductor and exists in three different crystalline structures: α-In_2S_3 (disordered defect cubic structure), β-In_2S_3 (defect spinel structure obtained in either the predictable cubic or tetragonal form), and γ-In_2S_3 (hexagonal structure) [11]. β-In_2S_3 is thermodynamically the mainly stable phase at room temperature. Furthermore, In_2S_3 polycrystalline films present highly transmittance (70–80%) in the visible and near infrared region and a band gap varying from 2 to 3 eV depending on chemical composition and technique deposition [12]. Barreau et al. [13] revealed that the existence of sulphide vacancies and indium interstitials in the β-In_2S_3 crystal can easily manner oxidation states on its surface. Ho et al. [14] reported oxygen sensing actions by In_2S_3 due to formation of surface oxide of β-$In_2S_{3-3x}O_{3x}$. In the same way Bouguila et al. [15] have studied the effect of oxygen pressure on the electrical properties of In_2S_3 films by impedance spectroscopy at room temperature. They showed a reproducible change in electrical conductance from vacuum (10^{-3} Torr) to air which is governed by physisorption of oxygen molecules at the sample surface. The dependence of its conductance on oxygen adsorption and desorption shows that In_2S_3 film is potential material for gas sensor applications. In this work, we investigated the physical properties of sprayed β-In_2S_3 films. The In_2S_3 polycrystalline films were studied in needs of their response magnitude as a function of operating temperature using DC electrical characterization to check the sensitivity of the films to ethanol vapor.

2. Experimental

In_2S_3 films were grown on glass substrates by Spray Pyrolysis. This technique is simple and low cost method for the deposition of large area thin films at moderate temperatures (100–500 °C), does not require high quality targets or vacuum, and permit an easy control of composition and microstructure; it's a facile way to dope material by merely adding doping element to the spray solution. We have used indium chloride $InCl_3$ and thiourea $SC(NH_2)_2$ as material precursors. The solution and nitrogen gas flow rates were

* Corresponding author.
E-mail address: Ahmed_laabidi@yahoo.fr (A. Labidi).

https://doi.org/10.1016/j.snb.2018.01.175
0925-4005/

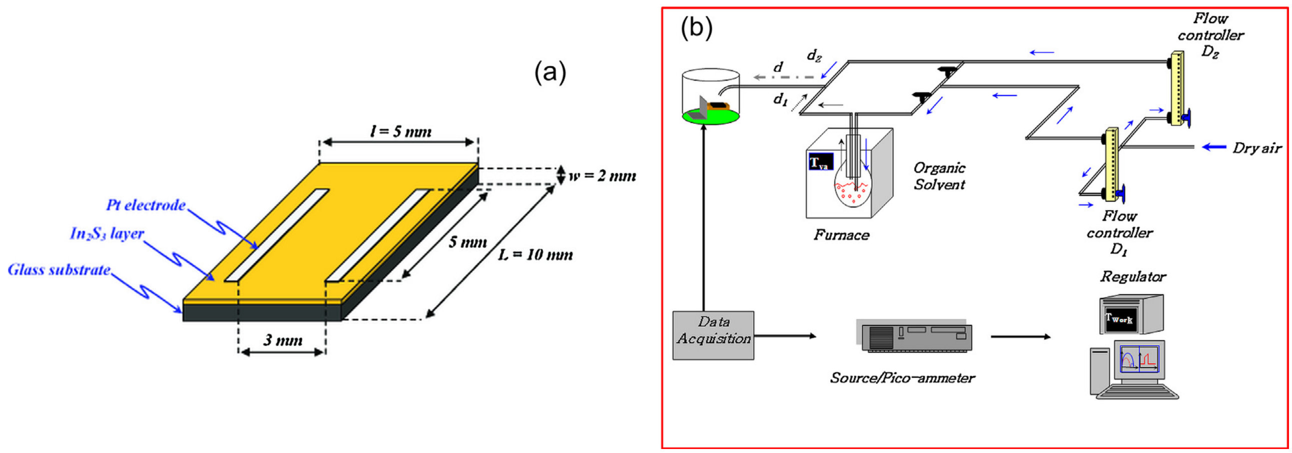

Fig. 1. (a) Configuration of In_2S_3 sensor, (b) Experimental set-up used for ethanol vapor detection.

kept constant at 2 ml min^{-1} and 6 l min^{-1}, respectively. The S/In molar ratio in the precursor solution and the deposition time (t_d) were fixed at 2 and 20 min, respectively. The substrate temperature was fixed at 340 °C. The formation of In_2S_3 is given by the following equation:

$$2InCl_3 + 3SC(NH_2)_2 + 6H_2O \rightarrow In_2S_3 + 3CO_2 + 6NH_4Cl \quad (1)$$

The samples obtained have the shape of a parallelepiped, the dimensions of the glass substrate are (L = 10 mm, l = 5 mm, w = 2 mm) and the In_2S_3 film thickness is around 2 μm [15]. Two rectangular Pt electrodes 5 mm long and 3 mm apart are deposited on the surface of the film (Fig. 1(a)).

The crystalline structure of the films was analyzed by X-ray diffraction (XRD) using Cu-K$_\alpha$ radiation (1.5406 Å) of a Bruker D8 Advance diffractometer operating at 40 kV, 40 mA. Chemical analysis was performed by Energy Dispersive X-ray Spectroscopy (EDX). The surface morphology was investigated by way of Scanning Electron Microscopy (SEM). These films were also characterized using a JEM-200CX Transmission Electron Microscope (TEM).

The In_2S_3 sensing properties under ethanol were studied using the experimental set-up showed in Fig. 1(b). The adjustment of ethanol vapor partial pressure was attained using a two-arm gas-flow device; two mass flow controllers controlled the flow rate of the dry air used as carrier gas, in the range 1–5 l min^{-1} in both arms (d_1, d_2); dry air was charged with ethanol vapor by passing through a thermo-stated round-bottomed flask containing liquid phase. Ethanol was sent along the first arm. At the same time, dry air was sent along the second one; then both flows were mixed at the extremity of the two arms. The round-bottomed flask was placed in a Polystat cc1 Huber water bath in order to maintain a fixed temperature T_{vap}. In these conditions, a range of ethanol concentrations in dry air can be calculated by applying the following equation [16]:

$$[C](ppm) = \left(\frac{xd_1}{(1+x)d_1 + d_2}\right) \times 10^6 \quad (2)$$

where x is the vapor molar fraction in the flask at a fixed T_{vap}, given by:

$$x = \frac{P_{vap}}{P_{atm}} \quad (3)$$

with P_{vap} as the partial pressure of the vapor at a given temperature T_{vap}, and $P_{atm,}$ as the atmospheric pressure. By regulating d_1 and d_2 ($d_1 + d_2$ was kept constant at 1 l min^{-1}), diverse concentrations of ethanol in dry air can be obtained. The total flow charged with ethanol vapor was blown on the sensor placed in a test chamber and polarized at 0.5 V by a (HP4140B) source/pico-ammeter.

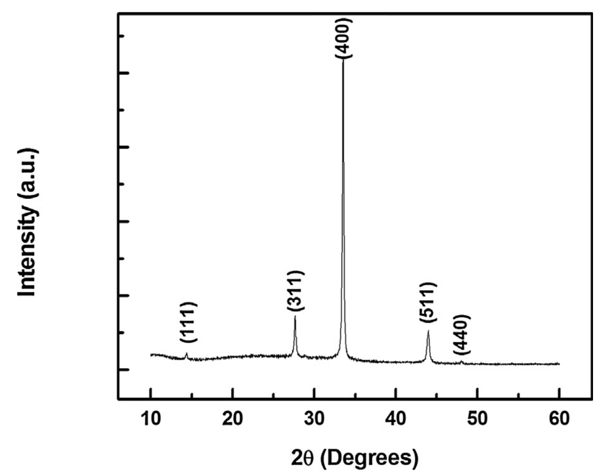

Fig. 2. XRD pattern of In_2S_3 thin film.

After a 5 min exposure to ethanol, the test chamber was purged for 15 min, which is the average time needed to go back toward initial baseline under dry air. Working temperature was varied in the range 250–400 °C.

3. Results and discussion

3.1. Structural, morphological and chemical composition

Fig. 2 depicts the XRD spectrum of sprayed In_2S_3 film, deposited at substrate temperature 340 °C. The diffractogram reveals (111), (311), (400), (511) and (440) peaks, which corresponds to cubic β-In_2S_3 phase according to the JCPDS card 00-032-0456, with preferred orientation along the (400) direction. The deduced lattice parameter "a" is about 10.73 Å. The High Resolution Transmission Electron Microscopy (HRTEM) image in Fig. 3 showed that the measured distance between the plans of the fringes is 3.15 Å, which is corresponding to the (311) plans of the cubic structure of In_2S_3 film. Such value is in accordance with XRD result as calculated to be 3.23 Å.

The In_2S_3 surface morphology was studied by Scanning Electron Microscopy (SEM) as shown in Fig. 4(a). SEM image reveals that the layer is adherent to the substrate, with no cracks and presents high porous percentage. Additionally, the film surface is dense and rough.

We have carried out energy dispersion X-ray Spectroscopy (EDX) measurements using a spectrometer attached to the scan-