Materials Science in Semiconductor Processing 71 (2017) 461–469

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Gas sensing applications of the inverse spinel zinc tin oxide

S. Hemmatzadeh Saeedabad[a], C. Baratto[b], F. Rigoni[b], S.M. Rozati[a,*], G. Sberveglieri[b], K. Vojisavljevic[c], B. Malic[c]

[a] Department of Physics, University of Guilan, Rasht, Iran
[b] SENSOR Lab, CNR INO & University of Brescia, Dept. of Information Engineering, Italy
[c] Jožef Stefan Institute, Electronic Ceramics Department, Ljubljana, Slovenia

ARTICLE INFO

Keywords:
Zn_2SnO_4 thin film
Acetone
Ethanol
Nitrogen dioxide
Gas sensor

ABSTRACT

In this work, we prepared zinc stannate (ZTO) thin films by RF sputtering starting from a sintered ceramic target with Zn:Sn ratio 2:1, by varying the argon/oxygen pressures during the deposition process. Thin films were deposited on alumina substrates at 400 °C, and subsequently annealed at 600 °C in the air. The transparency typical for the as-deposited films was preserved even after their annealing at 600 °C in the air, where the high temperature was crucial for the improvement of the crystalline Zn_2SnO_4, ZTO phase, as confirmed by Raman measurements. Additionally, the post-deposition thermal treatment resulted in porous ZTO films suitable for gas sensing application. The structural and surface morphological properties of thin films were investigated by Raman spectroscopy, field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX). Finally, the gas sensing properties towards nitrogen dioxide, ethanol and acetone have been tested, showing the high potentiality of this material as the gas sensor for ethanol and acetone at 400 °C, and nitrogen dioxide at 200 °C.

1. Introduction

Since the end of seventies, metal oxide based gas sensors have been proposed [1] as cheap and affordable tools to detect different target gases, like those responsible for air pollution (NO_2, CO, Volatile Organic Compounds) or gases that are indicative of the patient illness in breath test (acetone, ethanol) [2]. Among all metal oxides used as gas sensing materials, SnO_2 and ZnO are the most investigated and proposed in thousands of publications, due to their high sensitivity towards gases and ease of production through the physical or chemical techniques [3–8]. To fulfil the demand for more sensitive and selective sensors, many other oxides – binary compounds - were proposed, for example, In_2O_3 [9], WO_3 [10], CuO [11]. Ternary compounds, such as $CuAl_2O_4$ [12,13], $LaFeO_3$ [14] or Zn_2SnO_4 [13,15] can also be considered as an interesting choice for gas sensing applications. They are less popular than binary compounds, due to the challenges in obtaining the desired phase composition and its maintaining during the operation time of the sensor

Zn and Sn mixed oxide can crystallize into the inverse spinel phase - Zn_2SnO_4 (ZTO) and into the ilmenite $ZnSnO_3$ phase. Zn_2SnO_4 is an n-type semiconductor with a band gap of E_g = 3.6 eV. It was first proposed as an indium-free transparent conducting oxide (TCO) to replace Indium Tin Oxide (ITO) in solar cells applications [13], thanks to its high electron mobility and low visible absorption [16,17]. ZTO was also studied as sensing materials for chemical gas sensor [15,18–22]. Ilmenite phase was also considered for gas sensing, with lower performances than the inverse spinel Zn_2SnO_4 [23].

Several methods were used to prepare Zn_2SnO_4 gas sensors, such as thermal evaporation [18,19], spray pyrolysis [20,21] and hydrothermal method [15,24]. For industrial application, a highly scalable technique like sputtering is desirable. Sputtering process was used to prepare ZTO for gas sensing only starting from metal targets, due to the fact they are easily available on the market [22]. In the current work we addressed the RF sputtering deposition of sensing thin films starting from a home-made ceramic target of Zn_2SnO_4. The sintering process was controlled in order to obtain a ceramic target with the desired phase Zn_2SnO_4. We were the first that studied the influence of oxygen content during the deposition process on the functional properties of the obtained thin films. Morphological and structural parameters were investigated by SEM, EDX and Raman spectroscopy and correlated to the functional properties towards nitrogen dioxide, ethanol and acetone detection.

2. Experimental

The thin films were deposited by RF magnetron sputtering on various substrates, starting from a Zn-Sn-O target. The constituent oxides,

* Corresponding author.
E-mail address: smrozati@guilan.ac.ir (S.M. Rozati).

http://dx.doi.org/10.1016/j.mssp.2017.09.006
Received 26 March 2017; Received in revised form 12 August 2017; Accepted 2 September 2017

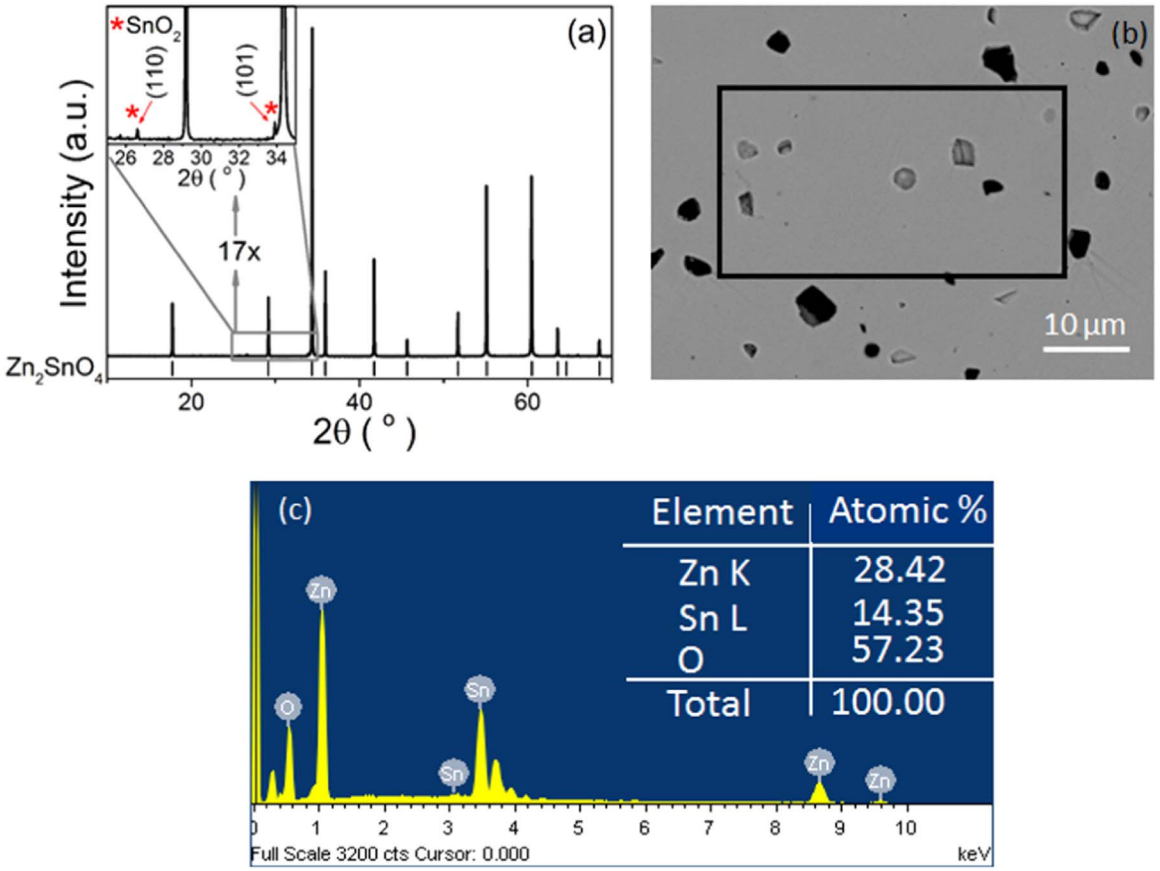

Fig. 1. XRD pattern (a), SE/BE micrograph (b) and EDXS result from the selected scan field (in (b) the black rectangle) (c) of the ZTO ceramic. Inset in (a) shows the 17× enlarged part of the pattern between 2θ 25° and 35°, where the most intense peaks of the SnO_2 are marked with a red star. The tick bars in (a) correspond to the peak positions of the cubic, Fd-3m Zn_2SnO_4 (PDF 01-074-2184). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Table 1
Sputtering atmosphere and temperature/time of annealing of the samples used for the gas test, Raman and SEM images presented in this work. The other deposition parameters were the same for all the samples: power = 100 W, time = 30 min, total pressure of the chamber = 5×10^{-3} mbar and the substrate temperature was 400 °C.

Sample	Atmosphere during the deposition	Temperature/time of annealing in air	Characterization in this work
A	100% Ar	As deposited	Raman
B	90% Ar + 10% O_2	As deposited	Raman
C	70% Ar + 30% O_2	As deposited	Raman
D	50% Ar + 50% O_2	As deposited	Raman
E	100% Ar	600 °C / 10 h	Raman/sensing/SEM
F	90% Ar + 10% O_2	600 °C / 10 h	Raman/sensing/SEM
G	70% Ar + 30% O_2	600 °C / 10 h	Raman/sensing/SEM
H	50% Ar + 50% O_2	600 °C / 10 h	Raman/sensing/SEM

ZnO (p.a. 99.99%, cat. no. 87812, Alfa Aesar Puratronic, Karlsruhe, Germany) and SnO_2 (p.a. 99.9%, cat. no. 12283, Alfa Aesar Puratronic, Karlsruhe, Germany) were mixed in a stoichiometric Zn:Sn = 2:1 M ratio (ZTO:Zn_2SnO_4), homogenized in a planetary mill (Retsch PM400, Retsch GmbH, Haan, Germany, zirconia vials and balls) in isopropyl alcohol and dried. Afterwards, the powder mixture was subjected to mechanical activation over a period of 48 h. That resulted in a partial amorphization of the powder mixture and subsequently enhanced reactivity and sinterability of the powders. The pellet of 68 mm in diameter was placed upon the ZTO powder bed to prevent contamination from the alumina crucible and sintered in oxygen to 1400 °C for 10 h. Zn_2SnO_4 was identified as the main phase by the X-ray diffraction (XRD) analysis, while the enlarged part of the pattern between 2θ 25° and 35° indicated the presence of SnO_2 in trace amount (see Fig. 1(a) and inset within). The scanning electron micrograph of the polished cross-section of the ceramic target taken in the back-scattered mode, SE/BE revealed a dense microstructure with closed porosity.

Note that the pores observed in Fig. 1(b), most likely resulted from the grain pull-outs during polishing. The elemental composition at the selected scan field analyzed by the energy-dispersive X-ray spectroscopy, EDX (Fig. 1(c)) confirmed the mean phase composition of Zn = 28.42 at%, Sn = 14.35 at%, and O = 57.23 at%, i.e. only a small variation in Zn and Sn atomic fractions, which not exceeding more than 0.2 at% from the stoichiometric composition (Zn = 28.57 at%, Sn = 14.29 at%, and O = 57.14 at%).

For XRD analysis of the drilled-off part of the ceramic target, the PANalytical diffractometer (X'Pert PRO MPD, Almelo, Netherlands, Bragg-Brentano geometry and CuKα radiation) was used to collect a diffraction pattern in the angular range 2θ = 10–70° with the step scan mode 2θ = 0.034° and integration time of 100 s. Microstructure and elemental composition of the polished cross-section of the sample were analyzed by the field emission scanning electron microscope, FE-SEM (JEOL JSM 7600F, Tokyo, Japan) operating in secondary electron imaging mode at 15 kV. The thin films were deposited on 3 mm × 3 mm alumina substrates for the SEM, XRD, Raman measurements and gas sensing characterization. The substrates were cleaned in acetone using ultrasound bath for 15 min and dried with synthetic air flow. During deposition the substrates were kept at high temperature (400 °C) to obtain crystalline thin films; previous investigation (unpublished) indicated that deposition between room temperature and 300 °C resulted in amorphous thin films, in agreement with results from literature [25]. The pressure during deposition was 5×10^{-3} mbar and the O_2/Ar ratio was modified in the range 0% to 50%. The RF power