Journal of Alloys and Compounds 634 (2015) 179–186

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Structural, optical and AC conductivity studies on alloy ZnO–Zn_2SnO_4 (ZnO–ZTO) thin films

R. Dridi [a], I. Saafi [a], A. Mhamdi [a], A. Matri [b], A. Yumak [c], M. Haj Lakhdar [a], A. Amlouk [a], K. Boubaker [a,*], M. Amlouk [a]

[a] Unité de Physique des dispositifs à Semi-conducteurs UPDS, Faculté des Sciences de Tunis, Tunis El Manar University, Tunisia
[b] Laboratoire de Physique des Matériaux, Département de Physique, Faculté des Sciences de Bizerte, Carthage University, 7021 Zarzouna, Tunisia
[c] Physics Department, Faculty of Arts and Sciences, Marmara University, 34722 Göztepe, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 10 December 2014
Received in revised form 30 January 2015
Accepted 1 February 2015
Available online 17 February 2015

Keywords:
ZnO–Zn_2SnO_4
Thin films
AC and DC conductivity
XRD analysis
Lattice Compatibility Theory (LCT)
Spray pyrolysis

ABSTRACT

This work deals with structural and electrical investigations on ZnO–Zn_2SnO_4 sprayed thin films grown on glass substrates at 460 °C. The structural, morphological and optical properties were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), and UV–visible spectrophotometry. XRD results describe the existence of the ZnO and Zn_2SnO_4 phases for various temperatures. AFM micrographs indicate the increase of roughness by increasing temperature. Finally, the electrical conductivity, conduction mechanism, relaxation model of these films was indeed studied by means of the impedance spectroscopy technique in the frequency range 5 Hz–13 MHz at various temperatures (220–280 °C). Besides, the frequency and temperature dependence of AC conductivity measurements, as well as Lattice Compatibility Theory (LCT) patterns, have been analyzed under the structural change framework when the annealing process is undertaken.

1. Introduction

Zinc oxide (ZnO) films have been widely studied because of their specific electrical, optical and mechanical properties, low material cost and relatively low deposition temperature. These films can be used in optoelectronic devices as transparent conducting oxide (TCO) [1]. Consequent research and enhancement led recently to more developed ternaries like Zn_2SnO_4 which is emerged as a new compound belonging to II_2–IV–VI_4 semiconductors family. It is a very promising material for various potential applications. In particular, the relatively high band gap energy (≈3.6 eV) [2] of ZTO renders it as an effective semiconductor material for photocatalytic applications [3–5], It finds extensive applications as gas sensors. Indeed, Sb-doped Zn_2SnO_4 sputtered thin films with spinel-type structure were deposited and showed good sensing characteristics to nitrogen dioxide until 300 ppm at 600 °C [6]. Recently, sensors based on Zn_2SnO_4/ZnO wire-sheet shape hetero-nanostructures networks have excellent gas sensing characteristics to hydrogen gas under 1000 ppm concentration below operating temperature of 300 °C [7]. In the same line, an enhanced NO_2 sensing property of Zn_2SnO_4-core/ZnO-shell nanorod sensors less than 5 ppm at 300 °C is reported [8]. This oxide material has been achieved as thin film [2,3,9] and as nano-forms [4,10] by many effective chemical techniques. Among these methods, the spray pyrolysis method is an attractive one due to its simplicity, safety, non-vacuum system of deposition, and inexpensive. Other advantages of this method are that it can be adapted easily for production of large-area films, and to get varying band gap materials during the deposition process.

Moreover, ac electrical investigations under structural change in such oxide occurring in some circumstances owing to experimental conductions (presence of defaults, dislocation, presence of binary phases such as ZnO and Sn_xO_y) remains the object of further investigations.

To address possible ways to control the structural as well as electrical conductivity in ZnO–ZTO sprayed thin films material, some works still pay attention to the possible causes of the change of its electrical behavior by using appropriate heat treatment under air atmosphere.

The present work aims at providing some structural and electrical investigations on alloy ZNO–ZTO thin films by means of AC conductivity measurements in terms of both temperature and frequency. This may be of great interest in some optoelectronic applications as well as in sensitivity tests as recently mentioned above.

* Corresponding author at: Faculté des Sciences de Bizerte, Carthage University, 7021 Zarzouna, Tunisia.
E-mail address: mmbb11112000@yahoo.fr (K. Boubaker).

http://dx.doi.org/10.1016/j.jallcom.2015.02.009
0925-8388/

2. Experimental conditions

Zinc stannic oxide thin films were deposited on glass substrates at 460 °C using appropriate mixture of two alcohol starting solutions (S_1 and S_2) containing Zn^{+2} and Sn^{+4} ions with 2:1 as ratio between molarities (S_1: 2×10^{-1} M; S_2: 10^{-1} M). This substrate temperature as well as the precursor composition solutions is selected according to protocols achieved previously in our laboratory [11,12]. Nitrogen was used as the carrier gas (0.35 bar) through a 0.5 mm-diameter nozzle. As reported previously, the nozzle-to-substrate plane distance was fixed at the optimal value of 27 cm. During the deposition process, the precursor mixture flow rate was taken constantly at 4 mL/min. To make the Electrical measurements we made contact with a platinum wire deposited on both side in a thin layer of ~1.5 cm^2 surface. These electrodes were painted on the two extremities of the sample using silver paste (Fig. 1). The measurements were carried out in the temperature range of 220–280 °C by using a tube furnace (Vecstar FURNACES) and the electrical conductivity was measured by HP4192A impedance for high frequency and Autolab PGSTAT30 for low frequency. Both devices are controlled by programs that allow received and safeguard measures.

3. Results and investigations

3.1. Structural properties

Fig. 2 shows the XRD patterns of alloy (Zno–Zn_2SnO_4) as deposited sprayed thin film grown on glass substrate at 460 °C and annealed thin films during 1 h in air at 500 and 530 °C. The observed indexed peaks in these XRD patterns are fully matched with the corresponding hexagonal würtzite structure ZnO and cubic structure Zn_2SnO_4 (PDF number: 24-1470) but the crystalline phase dominate is Zn_2SnO_4. The XRD results indicate that all the films have the polycrystalline structure. It is also seen that Zn_2SnO_4 exhibit preferential orientation of crystallites along (3 1 1) direction.

The average crystallite sizes of all Zn_2SnO_4 thin films are estimated from (3 1 1) principal peak by using the Debye–Scherrer formula [13].

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where $\lambda = 1.5418$ Å for Cu radiation, θ is the diffraction angle, $K = 0.9$, and β is the full width at half maximum FWHM with $\beta = \sqrt{\beta_e^2 - \beta_0^2}$, where β_e is measured from the film and is the full width at half maximum related to the instrument [13,14]. The calculated values of crystallite size are presented in Table 1. We note that the crystallites size increases by increasing annealing temperature, which results in the decrease of the grain boundaries.

The microstrain ε_s is calculated using the following relation [15]:

$$\varepsilon_S = \frac{\beta}{4\tan\theta} \tag{2}$$

This parameter increases by increasing annealing temperature due to the appearance of undesirable ZnO secondary phase with no negligible amount.

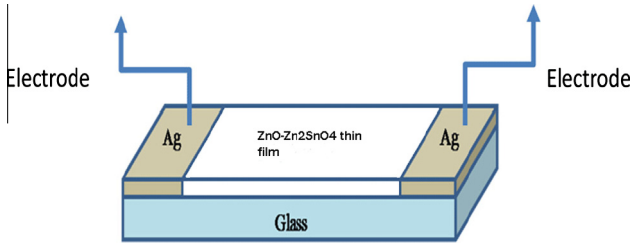

Fig. 1. Configuration of substrate/ZnO–Zn_2SnO_4 thin film/Ag samples for the electrical measurements.

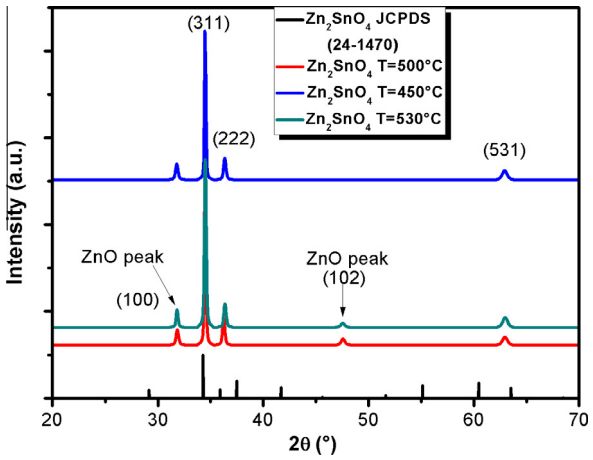

Fig. 2. XRD patterns of ZnO–Zn_2SnO_4 thin films deposited at different substrate temperatures.

Table 1
Lattice parameters, Grain size, dislocation density and micro strain for different samples .

	ZnO–Zn_2SnO_4 $T = 460$ °C	ZnO–Zn_2SnO_4 $T = 500$ °C	ZnO–Zn_2SnO_4 $T = 530$ °C
2θ (°)	34.49	34.46	34.45
β	0.167	0.117	0.115
$d_{(311)}$	2.600	2.602	2.602
a (Å)	8.62	8.63	8.63
D (nm)	49.85	71.14	71.19
ε (10^{-3})	0.23	1.6	1.6

3.2. Optical study

The optical transmission and reflectance spectra of (Zno–ZTO) films in the wavelength region of 250–2500 nm are shown in Fig. 3.

It can be seen that the interference fringe patterns are absent in transmittance and reflectance spectra due to weak multiple reflections at the interface. These film show a high transparency within the visible range with an average transmittance lying between 80% and 90%. The fundamental absorption edge of the films corresponds to transitions of electrons from the valence band to the conduction band edge and this can be used to calculate the difference in the optical band gap of the films. The absorption coefficient can be expressed by [16]:

$$\alpha = \frac{1}{d} \ln\left(\frac{1-R}{T}\right) \tag{3}$$

where $d = 0.5$ μm is the thickness of the prepared thin film.

In the case of a direct transition the absorption coefficient and optical band gap are related by the following relation which corresponds to the direct band gap [17]:

$$\alpha h\nu = \sqrt{A(h\nu - E_g)} \tag{4}$$

where A is a constant, $h\nu$ is the photon energy and E_g is the optical band gap. Fig. 4 shows the plot of $[\alpha\cdot(h\nu)]_2$ versus the photon energy $h\nu$ which yields in the sharp absorption edge for the high quality films by a linear fit it is clearly observed two band gap The first is ZnO $E_g = 3.3$ eV and the Second is ZTO $E_g = 3.7$ eV. This result is consistent with the XRD results.