Thermoelectric and photoconductivity properties of zinc oxide–tin oxide binary systems prepared by spray pyrolysis

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A R T I C L E   I N F O

A B S T R A C T

Zinc oxide–Tin oxide (ZnO–SnO) binary thin films were prepared on the glass substrates by spray pyrolysis method. The variation range of the molar ratio of x = [Sn]/[Zn] considered to be changed from 5% to 50%. The films characterized by using the X-ray diffraction (XRD) technique, UV–Vis–NIR spectroscopy, Hall effect, Seebeck effect, electrical and photoconductivity measurements. Using the scanning electron microscopy (SEM) and atomic force microscopy (AFM) images the morphology and roughness of the thin films surfaces were obtained, respectively. AFM micrographs indicate the decrease of roughness by increasing the dopant (Sn) concentration (x). XRD results describe the existence of the ZnO, SnO, SnO_2, $ZnSnO_3$ and Zn_2SnO_4 phases for various x values. The optical band gap and transmittance were obtained from UV–Vis–NIR spectroscopy results as a function of x. The results show a general band gap narrowing which occurs with the increasing of the Sn concentration which attributed to the structure and many body effects. Moreover, comparing to ZnO thin films, the remarkable decrease of the electrical conductivity and optical transparency were observed at the low x values. The conduction type was determined by the Hall effect and thermoelectric measurements. The Seebeck effect measurements show for $\Delta T \leq 185$ K, the electrons are the majority carriers, which replaced with the holes for $\Delta T > 185$ K. Power factor quantity was measured as a function of the Sn concentration and temperature. Furthermore, the power factor determines the best x value for the optimal electrical properties. Photoconductivity property was also observed in all samples which weakened for x ≤30%, and increased for the higher x values.

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1. Introduction

Transparent electronics is an advanced technology concerning the investigation and fabrication of the invisible electronic circuits. In order to realize transparent electronic and optoelectronic devices, the transparent conducting oxides (TCOs) have been widely utilized. TCOs exhibit simultaneously high electrical conductivity and optical transparency in the visible band of the electromagnetic spectrum [1–5]. Because of the wide band gap [6] and low electrical resistivity, TCOs hold a great deal of promise for development of technology which leads to the applications in electronics and photovoltaic, catalysis [7] and gas sensors [8]. In addition, TCOs are used in optoelectronic devices such as solar cells [9], liquid displays [10] and light emitting diodes [10]. TCOs have already been commercialized and the most famous of them is indium tin oxide (ITO) which is usually used for its high transparency and low resistivity. However, doped Zinc oxide (ZnO) is considered as a replacement of ITO due to its nontoxicity and abundance. On the other hand, because of the presence of the native defects, undoped ZnO is an n-type wide and direct band gap semiconductor (3.37 eV at 300 K)

with a large exciton binding energy (60 meV) and strong luminescence emission in ultraviolet (UV) domain. These properties make it as a potential candidate for the application in solar cells technology [11], TCO thin film electrodes [12], diluted magnetic semiconductors [13] and nanopiezotronics [14]. Various chemical, electrochemical or physical deposition methods have been used to prepare ZnO [15–30] and binary systems containing ZnO thin films [31] but few results are reported concerning spray pyrolysis method, which is an inexpensive technique for large area coating on glass and ceramic substrates at atmospheric pressure. The prepared thin films are reasonably high quality films and chemically stable; for example, the bandgap of $Zn_{1-x}Mg_xO$ is tunable from 3.37 to 4.05 eV which makes conducting $Zn_{1-x}Mg_xO$ films more suitable for ultraviolet (UV) devices [32]. The larger band gap of these conducting layers with high carrier concentration could be fabricated by doping of $Zn_{1-x}Mg_xO$ with Al which is also desired in the modulation-doped heterostructures designed to increase electron mobility [33].

Doping can also be applied to make the physical properties such as thermoelectricity in ZnO [34]. Few reports are about the influence of Sn doping onto ZnO physical properties [35] or ZnO–SnO binary system [31]. Using the spray pyrolysis method, in this paper, the structural, optical, electrical, and photoconductivity properties of ZnO–SnO thin films are investigated. In addition, thermoelectric effect and its behavior via

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temperature gradient studied in the ZnO–SnO thin films, looking for the best Sn content for the optimal properties.

2. Experimental procedure

2.1. Preparation of thin films

Zinc oxide–tin oxide (ZnO–SnO) thin films were deposited on glass substrates. The initial spraying solution was 0.15 mol/l of zinc acetate, $(Zn(CH_3COO)_2 \cdot 2H_2O)$, and in 100 ml of solvent including double distilled water and 2-propanol in a volume ratio of 1:3 (25 ml water, 75 ml 2-propanol). For synthesizing the ZnO–SnO binary compound, the stannic chloride $(SnCl_4)$ with desired molar ratio (x = [Sn]/[Zn]) was added to the zinc acetate solution. Sn concentration (x values) was varied from 5 to 50%. To enhance the solubility of zinc acetate, a few drops of acetic acid were also added to the solution. Before deposition process, the substrates were cleaned with normal detergent and deionized distilled water and subsequently they rinsed with 2-propanol alcohol. Deposition procedure was done by spray pyrolysis techniques with the conditions mentioned in Table 1. For comparing, a sample of ZnO thin film was also prepared at the same conditions.

2.2. Characterization

For the structural studies of the films, X ray diffraction (XRD) patterns of the ZnO and ZnO–SnO thin films were recorded by D8 Advance Bruker system with Ni filtered CuK_α (λ = 0.15406 nm) radiation at an operating voltage of 35 kV and a current of 30 mA. Diffraction data was obtained over the range of 10–70° two-theta. Surface morphology was determined using a Phillips XL-30 scanning electron microscope (SEM) system with the operating voltage of 15 kV and the emission current of 40 mA. The surface roughness of the films was studied by using an atomic force microscopy (AFM) instrument (DME, model 95-50E) on contact mode. AFM image was acquired in ambient air and digitized in to 256 × 256 pixels.

The optical measurements were carried out in the wavelength range of 190–1100 nm using 4802 Unico double beam spectrophotometer. Film thickness was determined by using the Swanepoel method [36] and verified by AFM images. The direct band gap energy (E_g) of the prepared films was obtained from the extrapolation of the linear part of the $(\alpha h\nu)^2$ curve versus photon energy ($h\nu$) and using the Tauc equation [37],

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right), \tag{1}$$

where $\alpha, E_g, h\nu$ and A are the absorption coefficient, the band gap energy, the optical beam energy and a constant, respectively.

The sheet resistance (R_S) of the films was measured by two-point probe method using thermally evaporated aluminum electrodes. By using the measured thickness of the thin films and R_S data, the resistivity was calculated via following relation

$$\rho = R_s t, \tag{2}$$

where t is the thickness of the thin films. In addition, the carrier mobility μ was determined by the following relation,

$$\mu = \frac{1}{ne\rho}, \tag{3}$$

where n, e and ρ are the carrier concentration, charge of electron and resistivity, respectively.

The Hall effect measurements were performed at room temperature, a longitudinal voltage up to 15 V and a magnetic flux density (B) up to 150 mT perpendicular to the film plane were applied for evaluating the concentration and conductivity type of majority carriers. The majority carrier density was calculated using following equation [38],

$$N_{n,p} = \frac{IB}{|q|V_H t}, \tag{4}$$

where I, B, t, q and V_H are the measured current, magnetic flux density, the thickness of the films, electron charge and Hall voltage, respectively.

By applying a temperature gradient between the two ends of samples, the thermopower (emf) of the prepared films was measured and then the Seebeck coefficients (S) were determined by S = ΔE / ΔT equation [39]. Thermoelectric properties are described by the figure of merit (Z) equation [40]:
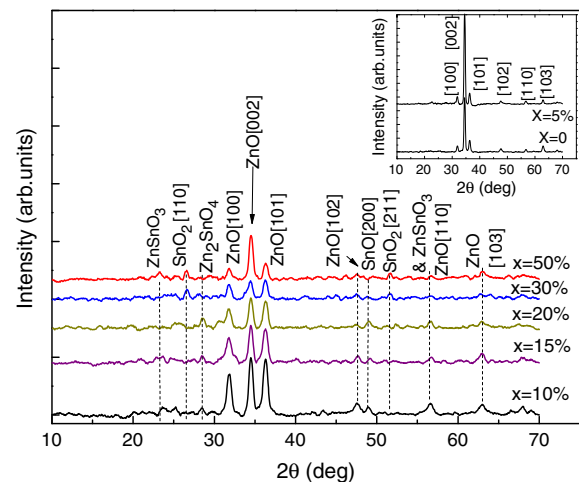
$$Z = \frac{\sigma S^2}{\kappa} \tag{5}$$

where σ is the electrical conductivity, S is the Seebeck coefficient and κ is the thermal conductivity, respectively. The term of P = σS^2 is known as power factor [41], which describes the quality of the electrical properties. To be a good thermoelectric material, it is required to have large power factor and low thermal conductivity.

To study of photoconductive properties of the samples, they were exposed by illumination with fixed intensity (4200 lx) at a fixed distance of 20 cm. The resistance of the films was recorded under lighting at specified time intervals during 15 min at room temperature.

3. Results and discussion

3.1. Structural properties

According to the procedure described in the previous section, Fig. 1 represents the XRD patterns of the ZnO–SnO thin films as a function of Sn concentration (x = [Sn]/[Zn]). In addition, Table 2 presents the details of XRD results as a function of x. As illustrated in Fig. 1, for the

Table 1
Spray deposition parameters.

Parameter	Specification
Substrate temperature (°C)	450
Solution volume (ml)	200
Solution flow rate (ml/min)	10
Nozzle to substrate distance (cm)	30
Carrier gas pressure (Pa)	3.5×10^5

Fig. 1. The XRD patterns of ZnO–SnO thin films versus 2θ for different Sn concentrations (x).