Materials Science in Semiconductor Processing 16 (2013) 2021–2027

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Influence of Sn content on properties of ZnO:SnO_2 thin films deposited by ultrasonic spray pyrolysis

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ARTICLE INFO

Keywords:
Thin films
TCO
Ultrasonic spray
II–VI Semiconductors

ABSTRACT

The present work is devoted to the preparation of zinc oxide (ZnO): tin oxide (SnO_2) thin films by ultrasonic spray technique. A set of films are deposited using a solution formed with zinc acetate and tin chloride salts mixture with varied weight ratio R=[Sn/(Zn+Sn)]. The ratio R is varied from 0 to 100% in order to investigate the influence of Sn concentration on the physical properties of ZnO:SnO_2 films. The X rays diffraction (XRD) analysis indicated that films are composed of ZnO and SnO_2 distinct phases without any alloys or spinnel phase formations. The average grain size of crystallites varies with the ratio R from 17 to 20 nm for SnO_2 and from 24 to 40 nm for ZnO. The obtained films are highly transparent with a transmission coefficient equal to 80%. An increase in Sn concentration increases both the effective band gap energy from 3.2 to 4.01 eV and the photoluminescence intensity peak assigned defects to SnO_2. The films electrical characterization indicated that films are resistive. Their resistivities vary between 1.2×10^2 and 3.3×10^4 (Ω cm). The higher resistivity is measured in film deposited with a ratio R equal to 50%.

1. Introduction

Metallic oxides thin films such as: In_2O_3, SnO_2, ZnO and CdO have been quite intensively studied during the last decades. When doped these oxides acquire two major properties: high transparency and metallic like electrical conductivity. This unique combination of properties results in the application of metallic oxides as transparent conducting oxides (TCOs) for optoelectronic devices. They found applications as transparent electrodes for flat-panel displays (FPDs), anodic electrode of organic light emitting device (OLED) [1,2], active channel layer of thin film transistors (TFTs) [3] and thin film solar cells [4]. During the Nineties, an intense research activity was devoted to TCOs thin films along with a variety of TCOs materials have emerged. In order to investigate TCOs appropriate to particular applications, new materials were actively studied, these last years, from simple metallic oxide to binary and ternary oxide compounds have emerged namely: Zn_2SnO_4 [5,6], $MgIn_2O_4$ [7–9], $CdSb_2O_6$:Y [10], $ZnSnO_3$ [11,12], $GaInO_3$ [13], $Zn_2In_2O_5$ [14], In_4SnO_{12} [15] and $AgInO_2$:Sn [16].

Numerous methods have been used for TCOs thin films preparation such as: sputtering, electron beam evaporation [17], chemical bath deposition [18], MOCVD [19], electroless bath deposition [20], PLD [21] and spray pyrolysis [22,23]. Spray pyrolysis technique is a very promising method due to its simplicity and economy with the advantage to prepare films at ambient atmosphere.

Many research works were focused on simple oxide systems like ZnO, SnO_2, In_2O_3, TiO_2… etc. However, very little attention was paid to binary oxides systems [24,25] like ZnO:SnO_2, ZnO:In_2O_3, SnO_2:In_2O_3, TiO_2:In_2O_3… etc.

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http://dx.doi.org/10.1016/j.mssp.2013.07.023

The present work reports on the investigation of the effect of Sn content on the structural, optical and electrical properties of ZnO:SnO_2 thin films prepared by ultrasonic spray pyrolysis at 300 °C.

2. Experimental details

ZnO:SnO_2 films were prepared by ultrasonic spray technique. The deposition system is a simple homemade apparatus (Fig. 1), the nozzle is feed from a solution container by simple gravity through a flow rate controller, and the arriving liquid is atomized by 40 kHz ultrasonic wave delivered from a generator (Sonics vibra-cell). The formed droplets have a uniform diameter of 40 μm. The distance nozzle-substrate is fixed at 5 cm. The spraying solutions were composed of 0.1 M concentration of dehydrate zinc acetate and dehydrate tin chloride dissolved in methanol. Various solutions were prepared with different ratio R defined as: [Sn]/([Zn]+[Sn]), R is varied from 0 to 100% by increasing the weight of added tin chloride in the solution in detriment of zinc acetate (for $R=0$ the prepared film is pure ZnO, while for $R=100$ the prepared film is pure SnO_2). Films are deposited on glass substrates heated at 300 °C; the deposition time was fixed at 5 min. The films thicknesses were determined by means of profilometer stylus displacement; the measured values are in the range 200–400 nm. The films structural properties were determined by DRX using a system Philips X Pert with a beam of Cu$K\alpha$ ($\lambda_{CuK\alpha}=1.5418$ Å). The crystallites size was calculated using a well-known Debye–Scherrer's formula [26]:

$$G=\frac{0.94\lambda}{\Delta(2\theta)\cos\theta} \quad (1)$$

where G is the crystallite size, λ (=1.54059 Å) the wavelength of X-rays used, θ and Δ (2θ) are the angle of diffraction and the broadening of diffraction line measured at half of its maximum intensity respectively. Films morphology was analyzed using scanning electron microscope (Hitachi FEG S4800).

The optical transmission in the UV–visible range is obtained using a spectrophotometer Shimadzu UV-3101. The band gap energy (E_g) of SnO_2 and ZnO phases was estimated by assuming a direct transition between valence and conduction bands from the expression [27]:

$$(\alpha h\nu)^n=\beta(h\nu-E_g) \quad (2)$$

where β is a constant, the exponent n is equal to 2 and 1/2 for direct allowed and indirect allowed transitions respectively. Since ZnO and SnO_2 are known to be a direct semiconductors, we have chosen the exponent $n=2$. E_g is determined by extrapolating the straight line portion of the spectrum to $\alpha h\nu=0$.

The films electrical conductivity was measured in a coplanar structure obtained with evaporation of two golden stripes on film surface.

For PL experiments, the excitation was obtained with a 200 W mercury arc lamp source, using the ultraviolet lines at 313 and 334 nm. The PL signal was analyzed by a monochromator equipped with a 150 grooves/mm grating and by a charge-coupled device camera detector cooled down to 140 K. The response of the detection systems was precisely calibrated with a tungsten wire calibration source.

3. Results and discussion

3.1. Structural properties

The XRD pattern of ZnO:SnO_2 thin films prepared at different weight ratio R are shown in Fig. 2. As can be seen all films, except for $R=100\%$, exhibit diffraction peaks assigned to ZnO phase. The diffraction patterns are composed with a strong peaks assigned to (0 0 2) diffraction plane accompanied with small peaks due to (1 0 1) and (1 0 0) diffraction planes of ZnO phase (according JCPDS36-1451 card). This indicates that the deposited film is formed with polycrystalline hexagonal wurtzite ZnO phase as soon as zinc precursor is added in the starting solution, even with a small amount. The peaks related to SnO_2 phase start appearing later, only beyond $R=30\%$. A small peak located at $2\theta=33.80°$ assigned to (1 0 1) diffraction plane of SnO_2 phase (according to JCPDS46-1088 card). At low ratio R ranged from 0 to 30%, the absence of SnO_2 phase suggests that the added Sn atoms acts as donor doping of ZnO phase, this is comforted by the low measured electrical resistivity of films prepared in this ratio range (see Fig. 9). The dominance of ZnO phase even for higher ratio R is due to the fast and easy oxidation of zinc by comparison to tin.

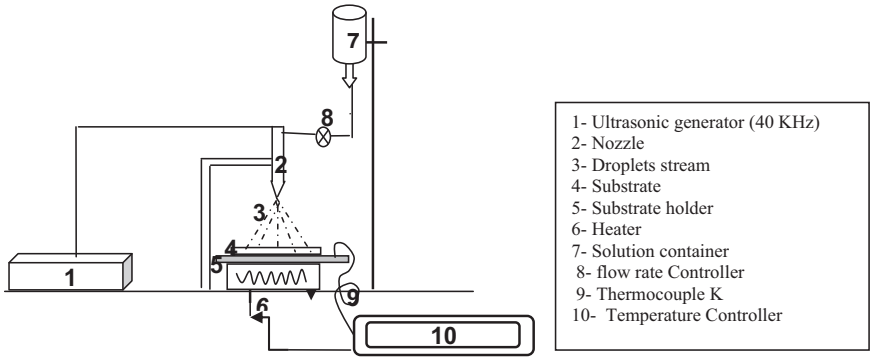

Fig. 1. Experimental set-up schematic drawn of the used spray deposition system.