Thin Solid Films 558 (2014) 283–288

Contents lists available at ScienceDirect

Thin Solid Films

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

# Structural and optical properties of ZnO–$SnO_2$ mixed thin films deposited by spray pyrolysis

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ARTICLE INFO

*Article history:*
Received 27 March 2013
Received in revised form 31 January 2014
Accepted 5 February 2014
Available online 15 February 2014

*Keywords:*
Zinc oxide
Tin oxide
Mixed thin film
Spray pyrolysis
Substrate temperature

ABSTRACT

Nanocrystalline ZnO–$SnO_2$ mixed thin films were deposited by the spray pyrolysis technique at various substrate temperatures during deposition. The mixed films were prepared in the range of 20.9 at.% to 73.4 at.% by altering the Zn/(Sn + Zn) atomic ratio in the starting solution. Morphology, crystal structures, and optical properties of the films were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and ultraviolet–visible and photoluminescence (PL) spectroscopy. XRD analysis reveals that the crystallinity of the Sn-rich mixed thin films increases with increasing substrate temperatures. FESEM images show that the grain size of mixed thin films is smaller compared to that of pure ZnO and $SnO_2$ thin films. A drop in the thickness and optical bandgap of the film was observed for films fabricated at high temperatures, which coincided with the increased crystallinity of the films. The average optical transmission of mixed thin films increased from 70% to 95% within the visible range (400–800 nm) as the substrate temperature increases. Optical bandgap of the films was determined to be in the range of 3.21–3.96 eV. The blue shift in the PL spectra from the films was supported by the fact that grain size of the mixed thin films is much smaller than that of the pure ZnO and $SnO_2$ thin films. Due to the improved transmission and reduced grain size, the ZnO–$SnO_2$ mixed thin films can have potential use in photovoltaic and gas sensing applications.



## 1. Introduction

In recent years, zinc oxide, tin oxide, and the combination of zinc and tin oxides received considerable attention from the research community. These are transparent conductive oxides (TCOs), with potential applications in numerous fields due to their unique physical and chemical properties. Potential fields of their applications include transparent electrodes [1], optoelectronic devices [2], piezoelectric devices [3], gas sensors [4], photocatalysts [5], and dye based solar cells [6]. Zinc oxide (ZnO) is an n-type wide direct bandgap ($E_g$ = 3.2–3.43 eV) semiconducting material with a large exciton energy of 60 meV, and possesses a hexagonal wurtzite crystal structure. Tin oxide ($SnO_2$) is also an n-type semiconducting material with a wide bandgap ($E_g$ = 3.6–3.97 eV) and a tetragonal rutile crystal structure [7].

Binary metal oxide systems such as ZnO–$V_2O_5$ [8], ZnO–$SnO_2$ [9], $In_2O_3$–$Sc_2O_3$ [10], CdO–ZnO [11], and $SnO_2$–$ZrO_2$ [12] have been studied in detail in the past few decades. Among them, ZnO–$SnO_2$ thin films have been of particular interest because of their suitability in applications, e.g., gas sensing and TCO in solar cells. ZnO–$SnO_2$ have been fabricated by various methods, such as RF magnetron sputtering [13], spray pyrolysis [14,15], sol–gel [16], filtered vacuum arc deposition [17–19], and pulsed laser deposition [20]. Among the methods used, spray pyrolysis is a relatively simple and cost-effective method. It basically comes under the category of a chemical solution deposition technique [21]. It has certain advantages such as the ability to produce films with large areas, shorter processing time, good adhesion, and the requirement of simple equipment. In this method, a fine mist of very small droplets of the aerosol (precursor solution) containing the desired species is produced. The droplets experience evaporation of the solvent during the transport to the pre-heated substrate. After droplet reached the substrate, thermal decomposition takes place on the hot substrate surface. This is followed by the formation of a continuous film. Substrate temperature is one of the most important parameters that determine the morphology and crystallinity of the thin films [22].

By spray pyrolysis, Bagheri-Mohagheghi and Shokooh-Saremi [15] fabricated ZnO–$SnO_2$ thin films with initial solutions of $SnCl_2$ and $ZnCl_2$. The films were fabricated by changing the Zn content from 0 to 30 at.%, and sprayed at a substrate temperature of 480 °C. Martinez and Acosta [14] prepared mixed thin films using $SnCl_2$ and $ZnCl_2$, and determined the effect of fluorine on their conductivity. Effect of fluorine was reported in mixed thin films by changing the substrate temperature from 350 °C to 500 °C, with a constant mixed atomic ratio of Zn/Sn = 0.40 in the precursor solution. In the present work, we vary the substrate temperature and mixed atomic ratio of Zn and Sn in the precursor solution which contains zinc acetate and $SnCl_4$ in ethanol. This is a new precursor solution that has yet to be reported in literature.

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http://dx.doi.org/10.1016/j.tsf.2014.02.022
0040-6090/