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Short communication

Conductivity enhancement of ZnO:F thin films by the deposition of SnO_2:F over layers for optoelectronic applications

R. Anandhi, K. Ravichandran*, R. Mohan

Post Graduate and Research Department of Physics, A Veeraiya Vandayar Memorial Sri Pushpam College (Autonomous), Poondi, Thanjavur 613 503, Tamil Nadu, India

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ABSTRACT

Fluorine doped tin oxide (SnO_2:F – FTO) layer is deposited over fluorine doped zinc oxide layer (ZnO:F – FZO) so as to get FTO/FZO bilayers with varying thickness proportions of the two layers using a simplified spray pyrolysis technique. In order to analyse the possible enhancement in the transparent conducting properties of these bilayered films, two separate sets of single layered FTO and FZO films are prepared with similar thickness values and their electrical, optical, photoluminescence and structural characteristics are compared with their bilayered counterparts. The electrical studies revealed that the double-layered films with the lesser thickness of FTO exhibit higher sheet resistance (R_{sh}) and the R_{sh} value decreases with the increase in the thickness of FTO over layer. The FTO/FZO bilayer with thickness proportions of FTO:FZO nearly equal to 450 nm:300 nm (3:2) is found to have good figure of merit (quality factor) when compared with FZO films. Even though the optical transmittance (T) in the visible range of FTO/FZO bilayer is lesser (80%) than that of FZO (90%) and FTO (85%) films, the electro-optical properties are reasonably good for the bilayered films making them suitable candidates for opto-electronic applications. The photoluminescence studies support the results obtained in the electrical and structural studies.

1. Introduction

Owing to the increasing demand for low-cost and high-performance optoelectronic devices, recently, intense research activities have been directed towards transparent conducting oxides (TCOs) especially doped and undoped zinc oxide films due to their multifunctional properties [1–4]. Among all the TCOs, zinc oxide [5,6] has emerged as one of the most promising materials, due to its unique combined electrical and optical properties [7]. In spite of its good optical transparency and electrical conductivity, the electrical properties of doped zinc oxide films deteriorate, if the deposition temperature is greater than 250 °C [8]. One of the other widely used TCOs *viz.* the fluorine doped tin oxide (FTO) film on the other hand has good thermal and chemical stability as observed by Fukano and Motohiro [9] and Bilgin et al. [10]. In this context, a novel FTO/FZO bilayer TCO is deposited with different thickness proportions of FTO and FZO onto glass substrates and their transparent conductive properties are studied systematically and reported in this paper. Report on the FTO/FZO bilayer, both prepared by spray pyrolysis, is not available in the literature, even though several researchers reported the enhanced TCO characteristics of bilayers involving doped and undoped zinc oxide and tin oxide films. For example, Alver et al. [11] deposited ZnO thin films on FTO coated glass substrates by spray pyrolysis technique and Vaezi [12] prepared SnO_2/ZnO double layer by employing sol–gel and two stage chemical deposition (TSCD) techniques. Similarly, Benhaliliba et al. [7] reported the comparative study on the characteristics of ZnO:In/SnO_2:F and ZnO:Al/SnO_2:F bilayers and Montero et al. [8] investigated the properties of ZnO:Al/SnO_2:Sb bilayers. Herrero and Guillen [13] found that by inserting a thin ZnO layer in the ITO film, the electrical resistivity can be reduced as compared to that of a single ITO film with similar optical transmittance. In the present study, FTO/FZO bilayers are fabricated employing a simplified spray technique, using perfume atomizer. To the best of our knowledge this is the first report on FTO/FZO bilayer, fabricated by this simplified spray technique. The structural, electrical and optical properties of the bilayered FTO/FZO films having different thickness proportions of FTO and FZO layers are compared with that of their single layered FTO and FZO counterparts.

2. Materials and methods

The FTO and FZO layers with a thickness more or less equal to 150, 300, 450, 600 and 750 nm (Table 1) were deposited separately onto glass substrates. Then, FTO/FZO bilayers with thickness proportions approximately equal to 150:600, 300:450, 450:300 and 600:150 nm (1:4, 2:3, 3:2 and 4:1) were deposited keeping the

* Corresponding author. Tel.: +91 04362 278602; fax: +91 4374 239328; mobile: +91 9443524180.
E-mail address: kkr1365@yahoo.com (K. Ravichandran).

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Table 1
Thickness and figure of merit (ϕ) values of FTO and FZO single layers.

Amount of precursor solution sprayed (mL)	FTO			FZO		
	Sample code	Thickness of the film (nm)	$\phi \times 10^{-2}$ $(\Omega/\square)^{-1}$	Sample code	Thickness of the film (nm)	$\phi \times 10^{-5}$ $(\Omega/\square)^{-1}$
10	T1	155	0.12	Z1	148	2.7
20	T2	297	0.12	Z2	309	1.4
30	T3	460	0.25	Z3	458	1.3
40	T4	608	0.11	Z4	597	0.7
50	T5	757	0.06	Z5	759	0.7

Table 2
Thickness proportions and figure of merit (ϕ) of FTO/FZO bilayer films.

Amount of precursor solutions sprayed (mL) (FTO precursor:FZO precursor)	FTO/FZO bilayer			
	Sample code	Approximate thickness proportions of FTO:FZO (nm)	Total thickness ratio	$\phi \times 10^{-2}$ $(\Omega/\square)^{-1}$
10:40	TZ1	150:600	1:4	0.004
20:30	TZ2	300:450	2:3	0.004
30:20	TZ3	450:300	3:2	4.240
40:10	TZ4	600:150	4:1	0.099

total thickness about 750 nm as given in detail in Table 2. For the FTO/FZO bilayers, FZO layer was deposited first onto the glass substrate as bottom layer and the FTO layer was deposited as the top layer (over layer). The host precursors used for the deposition of FTO and FZO layers were $SnCl_2{\cdot}2H_2O$ (0.1 M) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.2 M), respectively. For both the layers, NH_4F was used as dopant precursor. The fluorine doping level for the preparation of FTO and FZO layers was kept as 30 at.% [14] and 20 at.% [15], respectively, as these doping levels are optimum for obtaining good electrical results suitable for TCO applications. Deionised water, methanol and acetic acid were used as solvent with the ratio of 7:2:1, respectively. Borosilicate glass plates are used as substrates. The intermittent spray deposition followed in this study is two step procedure: a spray and a 5 s interval. Distance between the nozzle and the substrate (NSD) was kept as 30 cm and the spray angle with respect to the plane of the substrate was 45°. The spray rate was 0.16 mL/spray. The substrate temperature was maintained at $350 \pm 5\,^{\circ}C$ using temperature controller with chromel alumel thermo couple. The FTO, FZO and FTO/FZO samples are designated as T1, T2, . . . T5; Z1, Z2, . . . Z5; and TZ1, TZ2, . . . TZ5, respectively, as given in Tables 1 and 2.

The thickness of the films was measured using a profilometer (Surftest SJ-301). X-ray diffraction patterns were recorded using X-ray diffractometer (PANalytical-PW 340/60 X'pert PRO), which was operated at 40 kV and 30 mA with X-ray source of CuK_{α} radiation having wavelength 1.5406 Å. The sheet resistance (R_{sh}) values were measured with the use of four point probe. PerkinElmer UV–Vis–NIR double beam spectrophotometer (LAMBDA-35) is used to record the transmission spectra in the range of 300–1100 nm. Photoluminescence spectra were recorded using Spectro Fluorometer (Jobin Yvon_FLUROLOG-FL3-11) with Xenon Lamp (450 W) as the excitation source at room temperature.

3. Results and discussion

3.1. Structural studies

The X-ray diffraction patterns of the FTO and FZO films having gradually increasing thickness are shown in Figs. 1 and 2, respectively. The diffraction profiles revealed that the obtained peaks fit well with the tetragonal rutile [16] and hexagonal wurtzite structure [17] for FTO and FZO single layered films, respectively. The preferential or random growth of polycrystalline thin films can be

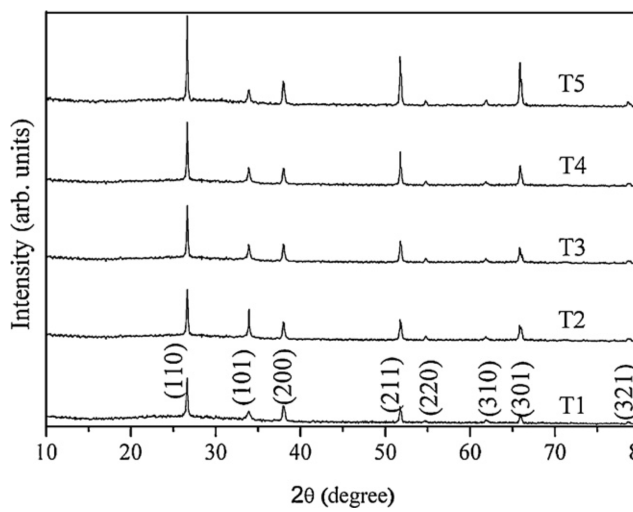

Fig. 1. X-Ray diffraction patterns of FTO single layered films with varying thickness.

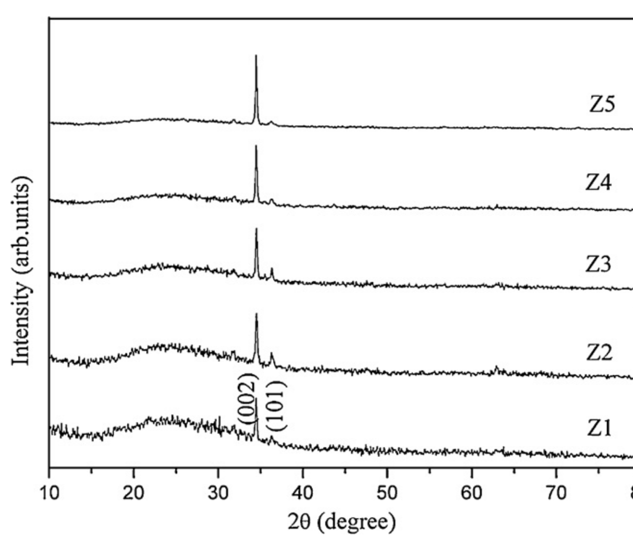

Fig. 2. XRD patterns of FZO single layer films showing textured growth with varying thickness.