Journal of Alloys and Compounds 588 (2014) 546–550

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

The role of electric field during spray deposition on fluorine doped tin oxide film

Anuj Kumar *, Sanjay Kumar Swami, Viresh Dutta

Centre for Energy Studies, Indian Institute of Technology, Delhi 110016, India

ARTICLE INFO

Article history:
Received 2 July 2013
Received in revised form 19 November 2013
Accepted 20 November 2013
Available online 27 November 2013

Keywords:
Transparent conducting oxide
Spray process
Electric field

ABSTRACT

The fluorine doped tin oxide film has been deposited on 10 cm × 10 cm glass substrate by using spray technique with a voltage applied between the nozzle and an annular electrode placed 2 mm below the nozzle. The effect of the electric field thus created during the spray deposition on structural, optical and electrical properties of SnO_2:F (FTO) film was studied. X-ray diffraction pattern revealed the presence of cassiterite structure with (200) orientation for all the FTO film. SEM study revealed the formation of smooth and uniform surface FTO film under the electric field over the entire substrate area. The electrical measurements show that the film prepared under the electric field (for an applied voltage of 2000 V) had a resistivity ~1.2×10^{-3} Ω cm, carrier concentration ~4.21×10^{20} cm^{-3} and mobility ~14.48 $cm^2 V^{-1} s^{-1}$. The sprayed FTO film have the average transmission in the visible region of more than about 80%.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Fluorine doped SnO_2:F (FTO) transparent conducting oxide (TCO) thin films are attractive for large area device (such as solar cell, and flat panel displays) applications because of high optical transparency in the visible region, good electrical conductivity and high infrared reflectivity. FTO films have been prepared by various techniques such as chemical vapor deposition, [1,2] spray pyrolysis, [3–10] vacuum evaporation, [11] reactive rf sputtering [12,13] and dc glow discharge [14]. In comparison to other deposition techniques, spray pyrolysis offers the following advantages: (1) high deposition rate, (2) excellent control of (overall) stoichiometry, (3) easy to develop as a continuous process, (4) high deposition efficiency and (5) easy coverage of large areas. Like other spray deposition techniques, the electrostatic spray deposition (spray under the electric field) technique usually atomizes a precursor solution into an aerosol, which is then directed to a heated substrate to deposit a thin layer. The history of applying the electrostatic spray deposition (ESD) process to deposit thin films is short, so that only a few reports exist concerning the deposition mechanism [15–22].

There are several physical and chemical processes involved in the ESD of layers, occurring either sequentially or simultaneously. Possible sequential steps are: spray formation; droplet transport, evaporation, disruption, preferential landing of droplets, discharge, droplet spreading, penetration of droplet solution, drying; surface diffusion, chemical reaction. All of these processes can influence the morphology and physical properties of the deposited layer. Particularly, since the smaller droplet size created due the electric pressure and Coulomb fission will result in faster solvent evaporation and smaller splat size. Shada et al. has reported the direct and indirect optical bandgap energies variation of tin oxide according the film thickness variation [23]. In spray process best film quality occurs only the high temperature deposition. Recently Athavan et al. deposited fluorine doped tin oxide on polyimide sheets at lower temperature by chemical method [24]. Ravichandran has used the FTO for conductivity enhancement of fluorine zinc oxide by the deposition of FTO/FZO bilayers [10]. The oxygen distributation along the depth in FTO film is reported by [25].

In this article we report on the successful spray deposition of FTO films on 10 cm × 10 cm substrate using a single nozzle under the electric field and the uniformity of electrical and optical properties of the deposited layer over the entire substrate is discussed.

2. Experimental details

The fluorine-doped tin oxide films were prepared on glass substrates by spraying a precursor solution which consists of 1.4 M $SnCl_4 \cdot 5H_2O$, 80% propanol and 2.7 M ammonium fluoride. Experimental setup for the spray deposition is described elsewhere [26].

The temperature of glass substrate during spray deposition was maintained at about 450 °C and the applied voltage was varied from 0 to 2 kV.

Nitrogen gas at a pressure of 2 kg/cm^2 was used as the carrier gas and the spray rate was ~ 1 ml/min. The distance from nozzle to substrate was 22 cm. The films were investigated by studying their composition, structural, optical and electrical properties. X-ray diffractometer (Phillips X'PERT PRO) was used to record X-ray diffraction (XRD) patterns of the films. Spectral transmittance and reflectance of the films was recorded in the wavelength range 300–2000 nm by using Perkin Elmer

* Corresponding author. Tel.: +91 9899486397; fax: +91 26591261.
E-mail addresses: anujkumarom@gmail.com, anujkumarom@rediffmail.com (A. Kumar).

0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.11.130

Lambda 1050 UV–VIS–NIR spectrophotometer. The surface morphology was observed using a Zeiss EVO-50 scanning electron microscope (SEM). The elemental composition was determined using energy dispersive spectrometer (EDS) system attached to the SEM. Electrical resistivity of the films at room temperature was determined with a Ecopia HMS-5000 Van der Pauw Hall effect measurement system. Four probe technique used for the sheet resistance mapping on the large area substrate. The thickness was measured by the Bruker Dektak XT surface profiler system.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the SEM images of the two layers deposited by applying 0 and 2 kV, respectively. It was found that the deposited layer for the applied voltage of 2 kV (Fig. 1b) looks denser than that for a zero electric field (Fig. 1a).

The roughness of the films was obtained as 55.30 nm and 13.46 nm without and with electric field, respectively. In normal spray deposition the larger droplet (~10 μm) size results in large splat formation and slower solvent evaporation. Hence large droplet size can create pinholes in the films. When an electric field is applied between the nozzle and the electrode for creating an additional electric pressure [27], the electrostatically charged droplets are propelled towards the grounded substrate. Then, a finer droplet size (<5 μm) [22] and also monodispersed size distribution [28] can be achieved. Hence, the earlier formed defects can be repaired in this way and a crack-free layer may be obtained. However, the deposition rate is decreased from 47 nm/min. to 34 nm/min. under the electric field. The rate of evaporation should also increase and the droplet size can be further reduced during transportation to the substrate. Two factors may lead to the observed reduction of the deposition rate: (1) the reduction of droplet shape and size and (2) the effect of fluorine incorporation on the film growth [29]. The electric field increases the droplet spreading in corona cone [30] which in turn enhances the uniformity of the film and helps in the larger deposition area. The uniformity in film thickness and sheet resistance with the electric field is clearly illustrated in Fig. 2. Clearly, a larger area of the substrate with uniform properties can be deposited by spray deposition under the electric field.

In order to investigate the role of droplet size and evaporation rate in FTO formation, the films are deposited at T_s = 450 °C with and without electric field, and the corresponding X-ray diffraction patterns are shown in Fig. 3. The polycrystalline film with (110), (200) preferential growth peaks are observed. Under the electric field deposition the peak corresponding the angle $2\theta = 54.55°$ [SnO_2 (220)], disappeared and FWHM of SnO_2 (110) peak is also changed under the electric field deposition. The peaks intensity corresponding the angles $2\theta = 61.85°$ [SnO_2 (310)], and $2\theta = 65.87°$ [SnO_2 (301)] were decreased after the electric field. After applying the electric field during spray deposition the preferential growths corresponding the plane (200) being produce, hence others peaks intensity are going to dimmest or disappeared. The lattice parameter is calculated by the standard formula $\frac{1}{d_{hkl^2}} = \frac{h^2+k^2}{a^2} + l^2/c^2$ where d_{hkl} interplanar spacing between parallel planes, a and c lattice constants. With electric field, the c/a axis of SnO_2 films is monotonically reduced from 0.674 Å (V = 0.00) to 0.670 Å (V = 2 kV), this reduction could be explained with the fact that in the SnO_2 host lattice, O^{2-} anions (ionic radius 1.4 Å) are replaced by F^- anions (ionic radius 1.33 Å). The crystallite sizes (D) are calculated by the Scherrer formula;

$$D = 0.9\lambda/(\beta \cos\theta) \quad (1)$$

where λ is the wavelength of X-ray radiation (1.54060 Å), β is FWHM in radians and 'θ' is the Bragg's angle of the concerning peak. The variation of grain size with electric field is shown in Fig. 4. The grain size of film is continuously decreases with increasing the electric field. Droplet shape is reduced during the transportation under electric field hence, the evaporation rate increases. Fast decomposition rate of propanol creates oxygen deficiency, which in turn increases the chance of more fluorine incorporation in the SnO_2 film. Fluorine electro-negativity is very high which may also reduce the nuclei size and can be responsible for further reduction in grain size. The residual stress also gives the information of structural properties in the film. The stress in thin films is expected due to differences in thermal expansion (thermal stress) and/or from the microstructure of the deposited film (intrinsic stress). The bi-axial residual stress in deposited SnO_2 thin films is calculated by using the following expression:

$$Strain = \frac{a_{film} - a_{bulk}}{a_{bulk}} \times 100\% \quad (2)$$

where a_{bulk}, a_{film} are the lattice constants of standard SnO_2 powder (a_{bulk} = 4.750 Å) and deposited films, respectively. The variation in strain (from −0.201 to −0.322) for SnO_2 thin films with electric field is shown in Fig. 4 the negative signs for estimated strain for the films indicated that the crystallites are under a state of compressive strain. With increasing electric field gradually, deficiency of oxygen atoms and incorporation of fluorine in crystal structure, resulting in the contraction of SnO_2 film and then the enhancement of the compressive strain in SnO_2 film.

3.2. Electrical properties

The variation of Hall mobility, carrier concentration and resistivity measurement at room temperature against the electric field is shown in (Fig. 5). The resistivity of FTO film decreases to 1.2×10^{-3} Ω cm with increase in voltage (2 kV). The trend of

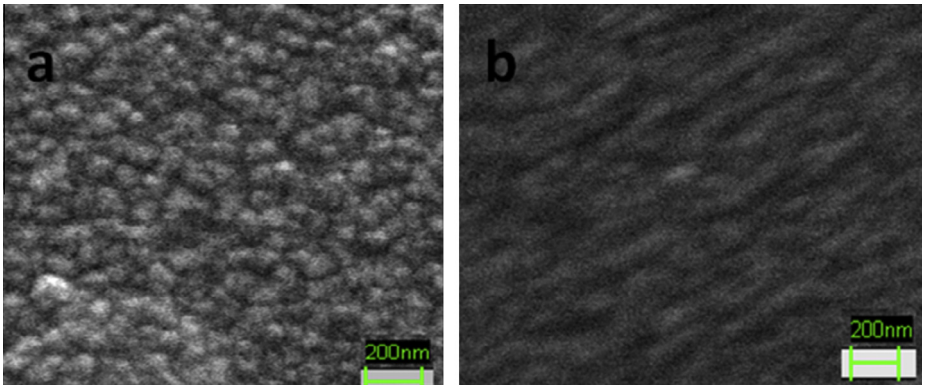

Fig. 1. Scanning electron micrographs of FTO films (a) without electric field and (b) with electric field.

Download English Version:

https://daneshyari.com/en/article/1612228

Download Persian Version:

https://daneshyari.com/article/1612228

Daneshyari.com