Superlattices and Microstructures 86 (2015) 186–197

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

Investigations on the crystalline, topographic, electrical and optical characteristics of doubly doped (Si + F) SnO_2 films deposited using spray pyrolysis technique

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ARTICLE INFO

Article history:
Received 29 June 2015
Accepted 1 July 2015
Available online 2 July 2015

Keywords:
Spray pyrolysis
SnO_2
Double doping
Structural properties
Electrical properties
Optical properties

ABSTRACT

Silicon and fluorine (Si + F) co-doped SnO_2 thin films were deposited on soda lime glass substrate using the spray pyrolysis technique. The Si and F doping levels were varied from 0–10 and 2.5–10 in steps of 2.5 at. %, respectively. Initially the optimum doping level of Si is found (7.5 at. %) at which the film exhibits the minimum electrical resistivity value ($4.23 \times 10^{-3}\ \Omega$ cm) and then the doping level of F is varied and it is found to be better at 10 at. % on which it offers lower resistivity of $1.96 \times 10^{-4}\ \Omega$ cm. From the structural studies, it is observed that the preferential orientation of all the films is along (2 1 1) plane irrespective of dopant and level of doping, but the peak intensity decreases as the doping level increases. The average transmittance of the all the films is found to be around 75% in the visible region and the optical band gap of the films are found to be in the region of 3.79–3.99 eV.

1. Introduction

Low resistive and high quality transparent conducting oxide (TCO) thin films have exceptional potential for the emerging technologies. For the past few decades SnO_2 based TCO thin films are gaining considerable attention in the new area of applications like optical, opto-electronic and biological domains [1–4] since, the non-stoichiometric undoped and doped SnO_2 exhibits better electrical conductivity and optical transparency in the visible region with direct band gap of $E_g \sim 3.6$ eV at room temperature. Previously various deposition techniques such as pulsed laser deposition, sol–gel, spray pyrolysis, sputtering, molecular beam epitaxy (MBE) have been applied to fabricate doped SnO_2 films [5–10]. Among these deposition methods, spray pyrolysis is a simple and inexpensive technique for large area coating.

In order to achieve better electrical and optical properties of SnO_2 thin films work has been done by changing the various process parameters and adding several dopants [11–16]. In the present work, Silicon and Fluorine co-doped SnO_2 films were fabricated on soda lime glass substrates using spray pyrolysis technique and their effect on the properties of SnO_2 thin films are discussed in detail. Generally, SnO_2 thin films exhibits *n*-type conductivity due to the presence of native defects i.e., non-stoichiometry (interstitial of tin (Sn_i) and oxygen vacancy (V_o)). Initially undoped and Si doped SnO_2 thin films were fabricated on soda lime glass substrates containing of large amount of Si. Thus Si doping can heal compatible the film and substrate, and hence the internal stress between film and glass substrate would be minimum, which can increase the

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http://dx.doi.org/10.1016/j.spmi.2015.07.005
0749-6036/

crystalline nature of the film. These can be effective in increasing electrical and optical properties. To the best of our knowledge, no systematic reports are available in literature on the influence of the different Si and F co-doping concentration on the crystalline, topographic, electrical, and optical properties of the SnO_2 films which is an effective way to tune the properties for optoelectronic applications.

2. Materials and methods

Undoped and doubly doped (Si + F) SnO_2 thin films were deposited onto the soda lime glass substrates using spray pyrolysis method. For that, GR grade chemicals were used in all the experiments. For preparing of SnO_2 thin films, 0.7 M of tin (II) chloride ($SnCl_2 \cdot 2H_2O$) was used as a source precursor and Si and F have been prepared by taking Hexamethydisilane ($C_6H_{18}Si_2$) and ammonium fluoride (NH_4F) as dopant precursors, respectively. These materials were dissolved in methanol and a few drops HCl were added to this solution and stirred for 2 h to get a homogeneous solution. Before the deposition process, all the substrates were thoroughly washed using diluted acetic acid and then cleaned with acetone using the ultrasonic cleaner. Finally they are rinsed in deionized water and dried in air. The substrate temperature was 500 °C and the nozzle to substrate distance (NSD) was kept as 30 cm and finally the flow rate of spray solutions were dialed and maintained as 3 mL/min. The crystalline structure of the films were analyzed using X-ray diffraction technique with (PANalytical-PW 340/60 X'pert PRO) using Cu Kα as anode type of X-ray source (λ = 1.5406 Å). The electrical characterization of the films were carried out using four point probe apparatus (vander Paw configuration) and Hall probe (ECOPIA HMS-3000) and the values are confirmed by the digital multimeter DMM 4050. The thickness of the films were measured using stylus technique (Profilometer: Surftest SJ 301) and weight gain method. The average thickness of the film is found to be in the range of 750 nm. The optical transmittance and photoluminescence spectra (PL) were recorded using UV–Vis–NIR double-beam spectrophotometer (Perkin Elmer lambda 35). The surface morphological properties were observed using atomic force microscope (AFM) (Veeco-di CPII). The experiments were repeated three times with the same optimum process conditions in order to confirm the reproducibility and repeatability and deviations in the values are within the acceptable limit. In this article, the samples of Si doped SnO_2 and doubly doped (Si + F) SnO_2 will be here after referred as STO and SFTO, respectively (Table 1).

3. Results and discussions

3.1. Structural studies

The crystal structure and single Si and double Si/F incorporation effect on crystalline features of SnO_2 are inquired with XRD analysis. Figs. 1 and 2 show the XRD patterns of the SnO_2:Si and SnO_2:Si:F thin films. All the films are exhibiting tetragonal rutile structure (JCPDS card no: 41-1445). In Figs. 1 and 2, the films are preferably grown along the (2 1 1) plane irrespective of the Si and F doping levels. The other peaks of (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 0), (2 2 0), (3 1 0), (1 1 2), (3 0 1), (2 0 2) and (3 2 1) are also found in XRD graphs.

The texture coefficient ($TC_{(hkl)}$) is identified by relation [17]

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_o}{\left(\frac{1}{N}\right)\sum I_{(hkl)}/I_o} \tag{1}$$

where I_{hkl} and $I_{o(hkl)}$ are observed intensity from XRD and standard intensity taken from JCPDS card no 41-1445, respectively and N is reflection number in XRD. The values of the texture coefficient are tabulated in Table 2. For pure and Si doped SnO_2 films, TC values of (2 0 0), (2 1 0), (2 1 1), (3 1 0), (2 0 2), and (3 2 1) peaks are greater than one, and this suggests that there are more crystal particles related to these peaks [18]. As soon as F atoms enter into SnO_2: Si structure, TC value of (2 1 0) abruptly increases to 9.18 values and then it fluctuates between the values of 6–9.

The mean crystallite size (D) and dislocation density (δ) values are evaluated by relations [19].

$$D = 0.9\lambda/\beta\cos\theta \tag{2}$$

$$\delta = 1/D^2 \tag{3}$$

Table 1
Sample code used in this work.

Si and F doping level in the SnO_2 thin films (at. %)	Sample name
Undoped	STO-0
2.5 + 0	STO-1
5.0 + 0	STO-2
7.5 + 0	STO-3
10.0 + 0	STO-4
7.5 + 2.5	SFTO-1
7.5 + 5.0	SFTO-2
7.5 + 7.5	SFTO-3
7.5 + 10.0	SFTO-4