Optik 127 (2016) 263–266

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Optical characterization of SnO_2 nanostructure thin films, annealed at different temperatures

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ARTICLE INFO

Article history:
Received 18 December 2014
Accepted 10 October 2015

Keywords:
SnO_2 thin films
Chemical spray pyrolysis
Annealing
Optical properties

ABSTRACT

SnO_2 nanostructure thin films were deposited on glass substrate at 450 °C by chemical spray pyrolysis (CPS) technique and then annealed at different temperatures; 450, 550 and 650 °C for 1 h. X-ray diffractions (XRD) of samples showed that grain size of thin films grows gradually from 48 nm for (as prepared sample) to 55 nm (for annealed at 650 °C sample). Transmittance spectra indicated that with increasing the annealing temperature up to 550 °C the transmittance is considerably decreased from 90% to ~83%, and then increases to 89% for the samples annealed at 650 °C. It is also found that the band gap is gradually decreases with increasing the annealing temperature. PL spectra are shown an intense and broad emission at 434 nm for as prepared sample and that annealed at 450 °C and 550 °C, and a weak broad peak for sample that annealed at 650 °C.

1. Introduction

Transparent conducting oxide (TCO) thin films; SnO_2, ZnO, TiO_2, CdO, In_2O_3 are of considerable interest in some of the important fields such as gas sensors, solar energy conversion, mechanical hard and high temperature resistant devices. Among these materials, the SnO_2 with n-type conduction and direct optical band gap of about 3.87–4.3 eV seems to be more interesting due to strong dependence of its electrical conductivity to gas adsorption [1,2]. SnO_2 nanostructures were fabricated in different forms; nanostructure thin films [3–5], nanowire and nanorod [6–11] and quantum dot [12–18]. Some researchers have studied the effect of substrates temperature on the grain size of nanostructure SnO_2 thin films. Shewale et al. [19] reported that crystallinity increases from 32 nm to 48 nm with the increase in the substrate temperature. A thick porous film composed of SnO_2 nanoparticles showed a gas sensitivity higher than sensors consisting of micron-size grains [3]. By mobility measurement results it was also found that the tin oxide film consisting of SnO_2 nanoparticles has a large influence on the conductivity [4]. In addition, SnO_2 transparent thin films are used in solar cells thin films as a window layer and also as a conducting electrode to collect the charge from active semiconductor layers [5]. High optical transparency and electrical conductivity simultaneously in thin films can be achieved by the proper preparation conditions such as the annealing temperature, dopants and controlled non-stoichiometry. Several investigations on the effect of annealing temperature on the electrical, structural and optical properties of SnO_2 thin films have been reported [20–22].

Various techniques have been used to deposit SnO_2 thin films such as chemical spray pyrolysis [23–28], chemical vapour deposition [23,29–32], sol–gel dip coating [33–36] sputtering [24,37–41] thermal evaporation [27,41]. In this paper we report the effect of annealing temperature on the crystalline structure and optical properties of the nanostructure SnO_2 thin films, prepared by CPS technique.

2. Experimental

The SnO_2 films were prepared by chemical spray pyrolysis (CPS) technique. In a typical method 11 g $SnCl_2{\cdot}5H_2O$ was dissolved in 5 mL of concentrated hydrochloric acid (HCl) by heating at 90 °C for 10 min. The resultant transparent solution was then diluted with methanol formed the starting solution. The microscopic glass slides with area of 75 mm × 25 mm and thickness of 1.4 mm, as the substrate, were cleaned by distilled water and organic solvents several times and then dried in vacuum. The solution was sprayed, through a stainless steel nozzle of 0.1 mm diameter, over the hot substrate by using the air as a carrier gas, so that it reaches to substrate in the form of very fine droplets. The distance between tip of nozzle and substrate was fixed at 30 cm, the substrate of 20 rpm/min plate rotation speed (for uniform deposition) was kept at 450 °C and the spray rate was maintained at 5 mL/min for 45 min.

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http://dx.doi.org/10.1016/j.ijleo.2015.10.033
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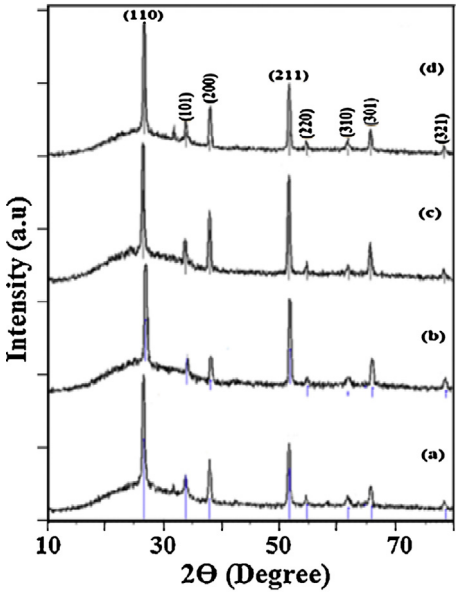

Fig. 1. XRD pattern of SnO_2 thin films: (a) as prepared annealed at (b) 450, (c) 550, (d) 650 °C.

The chemical reaction in the formation of SnO_2 thin film can be represented as:

$$SnCl_2 + 2H_2O \rightarrow SnO_2\downarrow + 2H_2\uparrow + Cl_2\uparrow$$

In this work the optical absorbance spectra of samples were obtained in the ultraviolet and visible regions (300–900 nm) using UV-Vis spectrophotometer (lambda 20, Perkin-Elmer). Crystal structure of samples was analyzed by X-ray diffraction (XRD, Bruker Advance D8 with CuK radiation in the range of 10–80°). Photoluminescence (PL) spectra of samples were obtained by using a fluorescent spectrophotometer instrument (fluorospectrophotometer, SPECTRO-96).

3. Results and discussion

Fig. 1 displays the XRD patterns of the fluorine-doped tin oxide thin films (with F/Sn = 15 wt.%) annealed at various temperatures (450–650 °C). It is clear that all samples having the polycrystalline nature with dominant peaks correspond to (1 1 0), (1 0 1), (2 0 0) and (2 1 1) planes of the tetragonal phase. It is also observed that the amorphous nature of the film decreases with increasing the annealing temperature. It is found that there is no significant change in the grain size of the films annealed at 450 and 550 °C whereas it increases considerably at 650 °C (Table 1). The average grain size of thin films were calculated by using the Scherrer formula [42]:

$$d = \frac{0.9\lambda}{\beta \cos\theta},$$

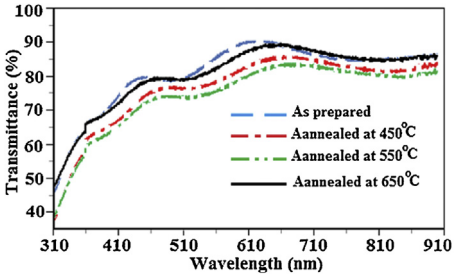

Fig. 2. Transmittance spectra of SnO_2 films.

where d is the average grain size, $\lambda = 1.542$ Å is the X-ray wavelength, β is the full width at half maximum (FWHM) of XRD peaks and θ is the diffraction peak position. It is found that there is no significant change in the grain size of films which annealed at 450 and 550 °C, whereas it increases considerably at 650 °C (Table 1). The increase in the size of the nanocrystals and the crystallinity at high annealing temperature (650 °C) can be attributed to enhancement of the kinetic energy of atoms at high temperature that assists more atoms move to more stable states in the lattice points.

Fig. 2 displays the transmittance spectra of SnO_2 thin films annealed at different temperatures. It shows that with increase in annealing temperature up to 550 °C the transmittance is considerably decreased from 90.5% (for as prepared sample) to ~83.8% (for annealed at 550 °C), and then increases to 89.7% (for sample annealed at 650 °C). The transmittance values are in agreement with the other reports [43,44]. The wavelength of two consecutive peaks (maximum transmittance) along with transmittance values (%) are shown in Table 1. The thickness of the thin films (t) can be calculated by using the wavelengths corresponded to two consecutive peaks in transmittance spectra (λ_1 and λ_2) and the following relation:

$$t = \frac{\lambda_1\lambda_2}{2(n_1\lambda_2 - n_2\lambda_1)}$$

where n_1 and n_2 are the corresponding refractive indices and can be approximated by $n_1 \approx n_2 \approx 2$ as follows:

$$t \approx \frac{\lambda_1\lambda_2}{4(\lambda_2 - \lambda_1)}$$

The results of the optical and structural measurements for F-doped SnO_2 films at annealing temperatures of 450 °C, 550 °C and 650 °C are summarized in Table 1.

Absorption spectra for SnO_2 thin films, at different annealing temperatures, are shown in Fig. 3. For all samples, the absorption at lower wavelengths in the UV region, 300–450 nm, is high and have low absorption at higher wavelengths, ~500–900 nm.

Fig. 4 shows the plots of $(\alpha h\nu)^2$ vs $h\nu$ at different annealing temperatures. The nature of linear part of these curves suggests the direct band gap for samples. The direct optical band gap (E_g) is determined by fitting the absorption data to the equation

Table 1
XRD and optical data for SnO_2 thin films annealed at different temperatures.

Annealing temp. (°C)	FWHM (°)	Grain size, d (nm)	E_g (eV)	λ_1 (nm) Transmittance (%)	λ_2 (nm) Transmittance (%)	Thickness (nm)
As prepared	0.335	48.7	3.56	455 80	623 90.5	422
450	0.337	48.4	3.49	497 77.1	664 86	494
550	0.345	47.3	3.41	491 74.3	665 83.8	469
650	0.304	53.7	3.40	48 79.7	659 89.7	445