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Annealing Effect on Nanocrystalline SnO_2 Thin Films Prepared by Spray Pyrolysis Technique

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ABSTRACT

In recent years, a transparent conducting oxide (TCO) SnO_2 semiconductor have gained considerable attention due to their potential application in gas sensors. More number of studies on TCO oxide have focused on the semiconducting metal oxides in which an intensive argument is that the transparent semiconductors. The SnO_2 thin films were deposited at 400 °C and then annealed at 500 °C and 600 °C and its structural, optical and electrical properties were characterized. The doping stoichiometric ratio was maintained as 4% and the resulting solution was sprayed on glass substrate which was kept at nozzle distance of 25 cm and the spray rate was 10 mL/min. The prepared pure SnO_2 thin films have been characterized by different methods such as XRD, FESEM, UV-Vis NIR and EDAX analyses. It was found that the nanocrystalline SnO_2 grains possesses structural features of the tetragonal rutile structure. Hence the prepared thin films are justified to be nanocrystalline and also the mean crystalline size decreased with respect to annealing temperature.

1. Introduction

Considerable research is being under process for the development of inexpensive nanocrystalline thin films of SnO_2. This is because tin oxide based thin films possess large bandgap *(Eg > 3 eV).* Scientifically and technologically n-type semiconductors are receiving a keen interest in modern research [1]. Due to its good optical properties such as transparency in visible light, reflectivity for infrared light, good electrical properties with low electrical sheet resistance, lead them to be a suitable candidate for a wide variety of applications such as gas sensors, adsorptive properties and chemical stability. It can be deposited onto glass, ceramics, SiO_2 and other substrate materials [2,3]. It has a high melting point and good transmission and hence it has a high specific volume and good cycling performance. Nano crystalline thin film samples are important subjects for investigation, as they are prepared under equilibrium conditions. Success in preparing such samples can provide valuable information on whether the observed sensing properties in nano crystalline thin film samples are indeed intrinsic properties of the materials [4,5].

Tin oxide thin film has been attracting interest for its applications on liquid gas sensors, solar cells and liquid crystals displays etc. Many methods such as spray pyrolysis, sputtering, molecular beam epitaxy and spin coating has been used to produce thin film. The spray pyrolysis process has some advantage over the other techniques due to excellent compositional control homogeneity at the molecular level due to the mixing of liquids precursors and lower crystallizations temperature. At the same time the spray pyrolysis of methods offers the possibility of preparing a small as well as large area coating of SnO_2 thin films at low cost for technological applications [6,7]. In this paper, the deposition and the characterization of SnO_2 were reported and studied the effect of annealing temperature on standard electrical and optical properties of SnO_2 thin films.

2. Experimental Methods

Pure SnO_2 thin films were deposited on glass substrate by the spray pyrolysis technique. All the chemicals used in this research were analytical grade and used without further purifications. As a starting material tin chloride $SnCl_4.5H_2O$ were used as precursor and was dissolved in ethanol and stirred four hours at 50 °C. The starting stoichiometry concentration of pure solution was maintained as 4%. Initially pure SnO_2 was sprayed on glass substrates at 400 °C. The spray rate and substrate to nozzle distance were maintained at 10 mL/min and 25 cm respectively. Then prepared samples were annealed at 500 °C and 600 °C. After synthesizing the films their structural, optical and electrical properties were characterized. The crystalline structure was carried out by a Rigaku X-ray diffractometer model DmAX 2200 with a copper anti-cathode (Cu Kα, λ=1.5Å) with an angle range (2θ) of 20-70°. The surface morphology, the cross-section and films thickness and composition of doping material were observed using a field emission scanning electron microscope (FE-SEM) with EDAX (FESEM: JEOL JSM 6701F) [8]. AFM images were obtained by using multimode scanning probe microscope CFM4000 Scanning Probe Microscope. The optical parameters were measured using a Shimadzu-UV-3101PC. Band gap (Eg) was evaluated from a plot of $(\alpha h\gamma)^2$ versus $h\gamma$ photon energy.

3. Results and Discussion

3.1 Structural Properties

The X-ray diffractogram of the pure SnO_2 thin film prepared at the substrate temperature of T_s = 400 °C and annealed at 500 °C and 600 °C are shown in the Fig. 1. The XRD pattern shows the preferred orientation at 2θ = 37.94° with the plane (200) confirmed the presence of SnO_2 with the tetragonal crystal structure as well as the observed other characteristics peaks with the plane corresponding to (110) and (211) which are well matched with standard data base values (JCPDS File No.46-1088). The appearance of characteristic peaks at different positions revealed that the thin films are in polycrystalline nature. It can be noticed that the intensity of the peak corresponding to (200) is increases upon the increase of temperature which implies the crystallization of the films. Furthermore, there is no any other additional peaks which are irrelevant to SnO_2. This is indicating the purity of the prepared thin films. The crystallite size of the prepared thin films were estimated using the following Secherr's Formula [9], $D = K\lambda/\beta\cos\theta$, where D is the crystallite size, K is a constant and its value is 0.9, λ is a wavelength of X-Ray beam used for diffraction, β is the full width at half maxima and θ is the diffraction angle. The crystallite size of the prepared thin films was calculated to be 48.8 nm and 16 nm corresponds to the annealing temperatures 500 °C and 600 °C respectively. Hence the prepared thin films are justified to be nanocrystalline and also the mean crystalline size decreased with respect to annealing temperature. This annealing temperature affect the crystallinity of the thin films.

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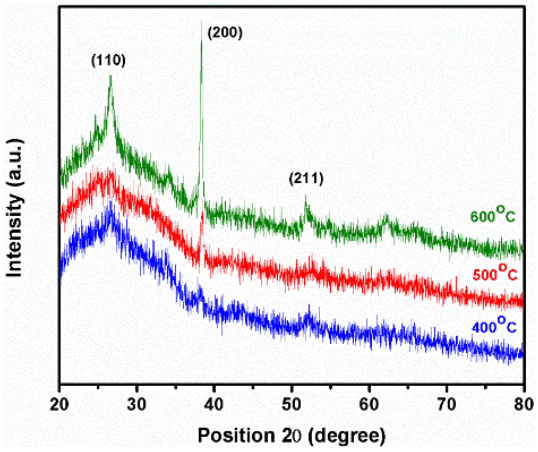

Fig. 1 XRD of SnO_2 thin films prepared at 400 °C, annealed at 500 °C and 600 °C

3.2 Morphology and Elemental Composition by FESEM and EDAX

Fig. 2 shows FESEM images of pure SnO_2 thin films prepared at the substrate temperature T_S= 400 °C and annealed at 500 °C and 600 °C respectively. It can be clearly seen from the FESEM images that the thin films have been formed with dense, crack-free and smooth nature with the presence of nano particles. These images are apparently showed the increase of particle size upon the increase of temperature. This is due to the grain growth as a consequence agglomeration of particles can took place. The approximate particle size was measured from the FESEM image and it lies in the range between 20 - 30 nm.

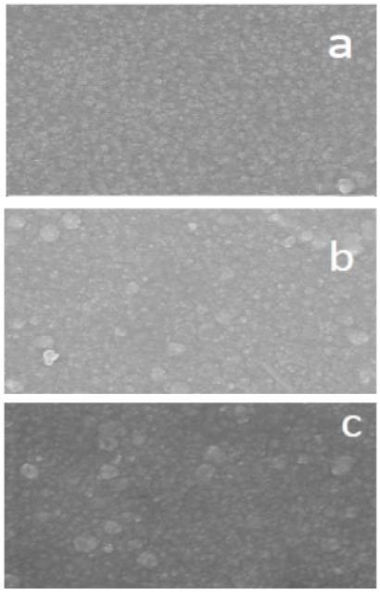

Fig. 2 FESEM micrograph of SnO_2 thin film prepared at 400 °C (a), annealed at 500 °C (b) and 600 °C(c)

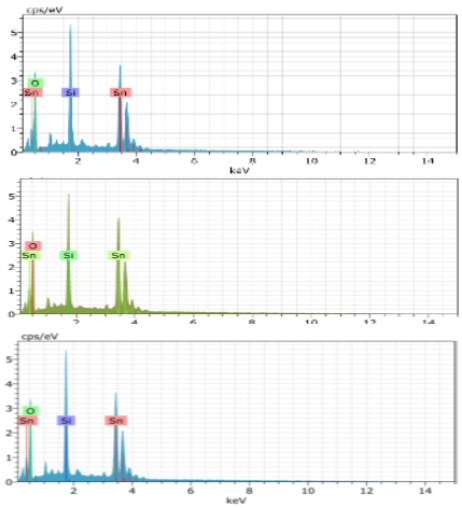

Fig. 3 EDAX spectrum of SnO_2 thin film prepared at 400 °C annealed at 500 °C and 600 °C

The Fig. 3 show the EDAX spectrum of the prepared SnO_2 thin films, showed an appropriate peak belongs to the elements Sn and O only. This is confirmed the purity of films which are free from any other contaminants. The peak at around 2 KeV was emerged from the substrate EDAX spectra substantiated of Sn and O elements in the prepared thin films. The other peaks are appeared due to the substrate.

3.3 Atomic Force Microscopy (AFM)

AFM images of SnO_2 nanocrystalline thin films prepared at the substrate temperature of 400 °C and annealed at 500 °C and 600 °C are shown in Fig. 4. The prepared thin film at T_s=400 °C shows the growth of crystallites from the inner towards the top of the surface and it seems like nanotips. This may be due to the evaporation of by products during the spraying and resulted into the formation of tip like topography. But after the annealing at 500 °C, the length of the tips seems to be decrease. Finally, increasing annealing temperature led to the agglomeration. The root means square roughness (Rms) values of the film determined [9]. The average crystallite size was estimated from the 2D image view and it is about 25 nm.

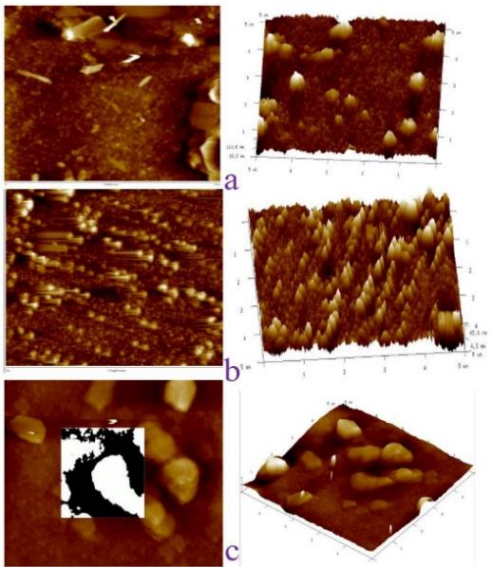

Fig. 4 AFM images of SnO_2 thin films prepared at 400 °C, annealed at 500 and 600 °C

3.4 Optical Properties by UV - Vis – NIR

The fundamental absorption corresponding to the optical transition of the electrons from the valence band to the conduction band can be used to determine the nature and values of the band gap (Eg) of the films. Depending on the characteristic property of the material, different theoretical equations have been used to calculate the absorption coefficient (α) value as a function of photon energy (hν). In this case, since the films are polycrystalline, the (αhν) curves correspond to crystalline material with direct allowed transitions (direct band gap) can be used to calculate the band gap by classical relation [10], $\alpha h\upsilon = A(h\upsilon - E_g)^n$, where E_g is the optical band gap. A is a constant and the exponent 'n' depends on the transition [11]. The UV-vis transmittance spectra of SnO_2 thin films deposited on glass substrate at prepared substrate temperature of 400 °C and annealed temperature of 500 °C and 600 °C are shown in Fig. 5.

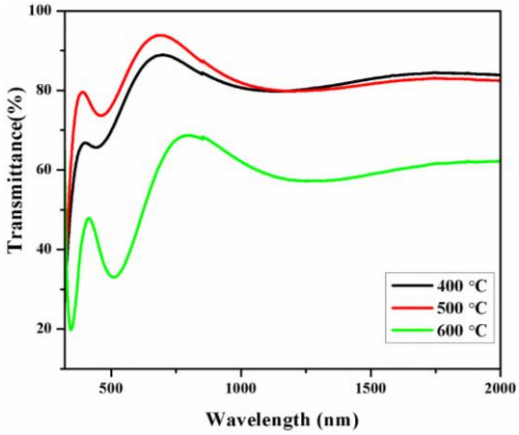

Fig. 5 Optical transmittance spectra of the SnO_2 thin films deposited on glass substrates

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The transmittance spectra revealed that the films are highly transparent in the visible region with the transparency of 85%, 95% and 70% for 400 °C, 500 °C and 600 °C annealed SnO_2 thin films respectively. An increase of annealing temperature to 500 °C led to enhancement of transparency, but further increasing the annealing temperature (600 °C) decreased the transparency of films, which may be caused by the increase of the density due to higher temperature effects. The Fig. 6 absorption edges are shifted from lower wavelength region to higher wavelength region (i.e., red shifted) is an indication of a decrease of the band gap of the SnO_2 thin films upon increasing annealing temperature.

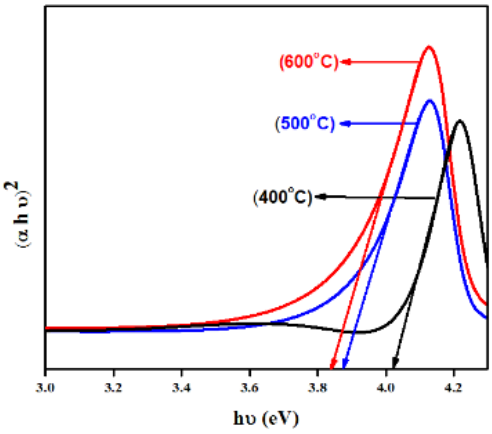

Fig. 6 Band gap of SnO_2 thin films deposited on glass substrates

4. Conclusion

The pure SnO_2 nanocrystalline thin film have been successfully prepared on glass substrate by spray pyrolysis method. Presence of SnO_2 was ascertained by XRD analysis. The crystallite size was calculated using Scherrer's formula and it was in the range of 48.8 to 16 nm. FESEM images demonstrated the fine and granular nanoparticles in the size range of 20 to 30 nm. EDAX spectra confirmed the presence of Sn and O elements. The prepared thin films have showed higher transparency (80 to 85 %) in the UV-visible spectrum. Therefore, it is clear that the prepared SnO_2 thin film may be a promising candidate for gas sensor applications. It was found that the nanocrystalline SnO_2 grains possesses structural features of the tetragonal rutile structure.

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