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Annealing Effect on Al doped SnO_2 Nano Structure Thin films Prepared by Spray Pyrolysis Technique

K. Pakiyaraj*

Department of Physics, A.P.A College of Arts & Culture, Palani – 624 601, Tamilnadu, India.

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ABSTRACT

Al-doped tin oxide (SnO_2) nanostructured thin films are prepared by homemade spray pyrolysis route on glass substrates prepared at 400 °C, and annealed at 500 °C and 600 °C. Using a solution consisting of $SnCl_4.5H_2O$ starting material and doping source was $AlCl_3$ with various Al doping ratio. $Sn_{1-x}Al_xO_2$ (x=0.08 to 0.10) were dissolved in ethanol and stirred four hours at 50 °C. The effect of changes in doping content and annealing effect of Al:SnO_2 nanostructured thin films was investigated. The result of X-ray diffraction have shown that the doped films are polycrystalline without any second phase with preferential orientations along the (110) and (200) planes and the grain size varied within range (3 nm-28 nm). The UV-Visible transmittance exceeds 85%, the optical band gap was estimated to be around 2.6 ev to 3.6 ev. The scanning electron microscopic (SEM) analysis showed the nanostructures consisting of small grains Nano flowers, Nano balls and Nano grains. EDAX to confirm the presence of dopant elements in the nanostructured thin films.

1. Introduction

Materials exhibiting high optical transparency, electrical conductivity and that can be grown efficiently as thin films, are widely used as transparent electrodes for various applications. Such as gas sensors [1], touch panel [2], corrosion resistant coating [3], anti-static coating on instrument panel [4], solar cell [5-7], organic light emitting devices (OLED) [8, 9], Heat mirror for energy efficient windows [10]. For these applications many transparent conducting oxide TCO films. Such as SnO_2, ZNO, TiO_2 and In_2O_3 must have wide band gap due to their strong chemical bonds, good optical transmittance in the visible region and low resistivity [11]. Tin Oxide (SnO_2) is one of the transparent conducting Oxide (TCO) material having wider band gap of 3.6 ev [12] and ionic radius is Sn^{4+} r = 0.71 Å [13]. To our knowledge undoped SnO_2 is an n-type semiconductor due to the presence of intrinsic defects like oxygen vacancies. Recent investigations have been focused on increasing n type conductivity of this material [14, 15], while both high quality n-and p type SnO_2 are essential for fabrication of SnO_2 based semiconductor devices. SnO_2 behaves as an n–type semiconductor, However when there is a suitable dopant doped with it, the carrier conversion takes place and change to P type semiconductor [16]. A lower valency cation as acceptor impurity such as Al^{3+} (ionic radius r = 0.51 Å) [13] in tin oxide decreases n type conductivity and increases the hole concentration and hence the p – conductivity. However, it is to be noted that in a successful acceptor doping process, besides doping level, effect of annealing and the atomic or cationic size of the acceptor dopant is very important. The current investigation was done on the fully transparent conductive sprayed Al: SnO_2 nanostructure thin films. The n type SnO_2 inverted to P type conductivity prepared by SPD was evidenced [13].

Al - SnO_2 thin films can be prepared by a number of methods such as CVD [17], Sputtering [18], Spray pyrolysis [19], Plasma and Sol- gel method [20] each of which has advantage and disadvantages. Spray pyrolysis is suitable for substrates with complex geometry and can be used for a variety of oxide materials. The advantages of Spray pyrolysis include [21] it can be easy and cheap since it is a non-vacuum process, substrates with complex geometries can be coated, leads to uniform and high quality coatings, low crystallization temperatures and porosity can be easily tailored. The pyrolytic spray technique is the most suitable when high visible transmission and high infrared reflectance are desired.

In this paper, we report the effect of Al doping percentage and annealing effect of films, variation on structural, electrical and optical properties of SnO_2:Al thin films prepared by homemade Spray pyrolysis technique.

2. Experimental Methods

Aluminium doped SnO_2 films were deposited onto the glass by spray pyrolysis technique. The starting material for Sn was ($SnCl_4.5H_2O$) and doping source was aluminium chloride ($AlCl_3$). Both precursor and doping compound were dissolved in ethanol. The starting doping ratio (Al/Sn) was 4% in the solution. The resulting solution were stirred four hour at temperature 50 °C, spray rate and substrate to nozzle distance were maintained respectively at 10 mL/min and 30 cm. The glass substrate was mounted on hot plate then heated to 400 °C which was controlled by dimmastrate and digital thermometer connected to the hot plate. Then prepared samples were annealed at 500 °C and 600 °C by muffle furnace. After synthesizing the films, their structural, optical and electrical characterizations were performed. The structural properties of our samples were carried out by a Rigaku X–ray Diffractometer model DMAX 2200 with a copper anticathode (CUKα, λ = 1.5 Å) with an angle range (2θ) of 20-70°. The optical parameters of the as – synthesized and annealed Al - SnO_2 films were measured using a shima DZU UV – 3101PC double beam spectrometer. The samples surface morphology was analyzed by the scanning electron microscopic Instrument JSM – 6360 and conformation of doping material by EDAX.

3. Results and Discussion

3.1 X – Ray Studies

Fig. 1 shows X – ray pattern of sprayed undoped (SnO_2) and doped (Al - SnO_2) at 400 °C as prepared temperature, 500 °C and 600 °C annealed temperature as a function of Al content. This spectra confirm the presence of tetragonal crystal structure in most sample and preferred direction along (110 and 200) planes. It is shown that the Al:SnO_2 films analyzed by X – ray in the 2θ – range of 20-70° are polycrystalline. The grain size was determined using the well-known Scherer formula [24], $D = 0.94\lambda/\beta\cos\theta$, where θ (rd) is half of Bragg angle λ (Å) is photon wavelength β (rd) is full width a medium height. The grain sizes were found to be 2 nm to 15 nm according respectively to strong (110) and (200) peaks. It was observed that the peaks base was broadened. It should confirm the nanostructures

*Corresponding Author: kpakiyaraj@gmail.com(K. Pakiyaraj)

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occurrence of the Al - SnO_2 sample. This was in well agreement with the SEM and EDX. Fig. 2 shows that Al doping content and annealing effect to reduce the grain size. The effect of Al doping on SnO_2 has been investigated by various researchers in the past [22, 23]. With increasing Al dopant and annealing temperature in the tin oxide film, the crystalline of SnO_2 decreased. Hence the doping element Al is a grain growth inhibitor.

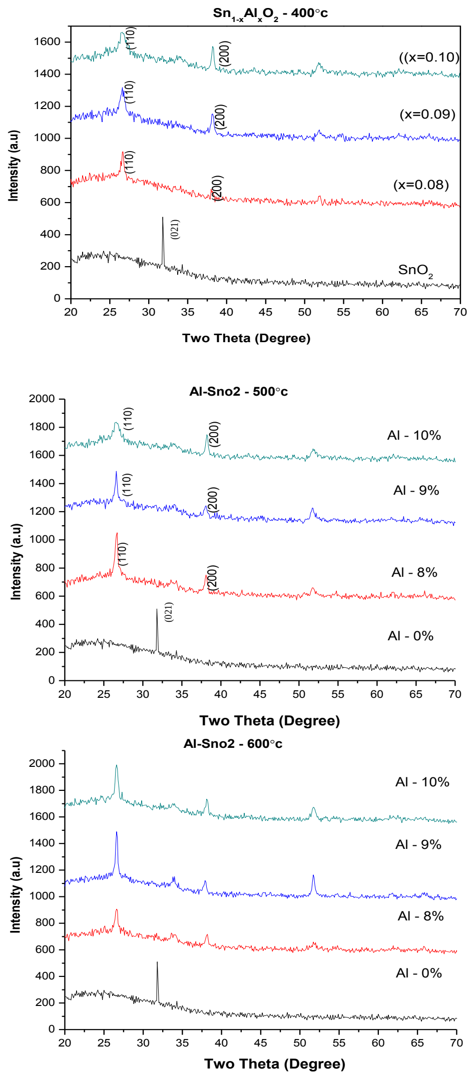

Fig. 1 XRD pattern of undoped and Al doped SnO_2 films deposited on glass substrates annealing at 400 °C, 500 °C and 600 °C

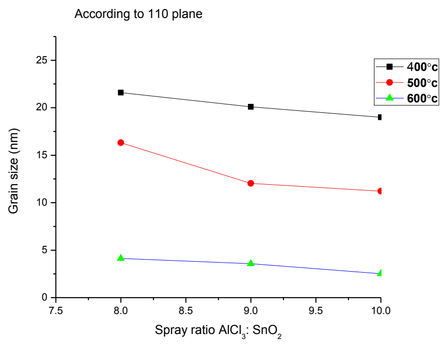

Fig. 2 Variation of grain Size with doping ratio and annealing temperature

3.2 UV-Vis and FTIR Characterization

Al doped SnO_2 thin film optical constants of the different atomic percentage and different annealing temperature are measured using UV transmission spectrum Fig. 3 show transmission of Al doped SnO_2 thin films with Al concentration (4% to 10%) and temperature 400 °C (prepared), 500 °C (annealing) and 600 °C (annealing). From the fig it is observed that the transmission of the film decreases with increase in Al concentration and annealing effect. The average percentage of transmission of all the thin film samples is lies between (25% - 85%) in visible region.

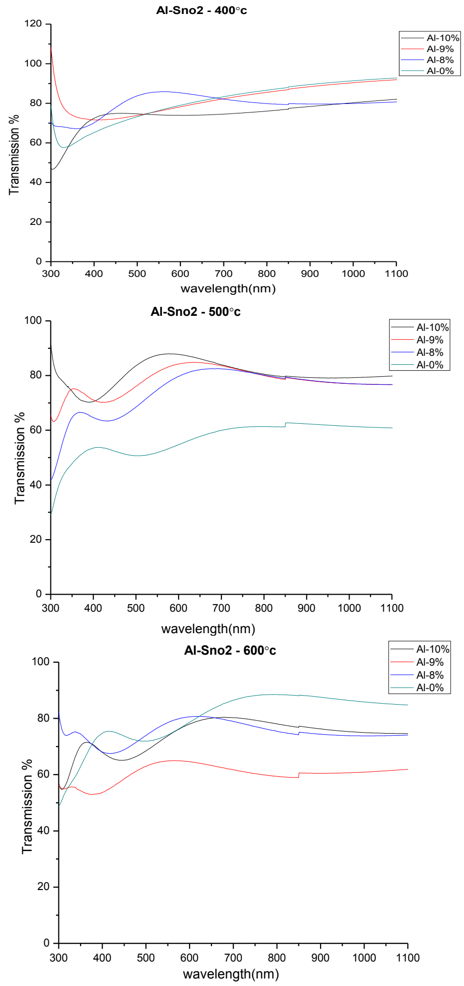

Fig. 3 Transmission spectrums of undoped and Al doped SnO_2 films deposited on glass substrates annealing at 400 °C, 500 °C and 600 °C

The optical band gap of the deposited Al - SnO_2 thin films are calculated by using the following formula [24], $(\alpha h\nu) = (h\nu - Eg)^{1/2}$, where α ($m^{-1}$) is the absorption coefficient h (J.S) is Planck"s constant ν (Hz) is the photon frequency Eg (ev) is the band gap energy. The optical band gap is determined by extrapolating of the linear part of the curve $(\alpha h\nu)^2$ vs. hν which intercepts the energy axis hν shown in Fig. 4 it is observed that the variation of band gap due to concentration of precursor solution and annealing temperature. The calculated band gap for 4% to 10% aluminium content at deposition temperature 400 °C (prepared), annealing at 500 °C and annealing at 600 °C. The calculated direct band gap values of Al - SnO_2 films lay in the range 3.62 ev to 2.63 ev for Al doped and un doped SnO_2 respectively. Which are also comparable with the values already reported 3.604 ev to 4.105 ev [25], 3.87 ev to 4.21 ev [23]. The band gap narrows down due to the decrease in the number of charge carriers with increasing in Al doping and annealing temperature.

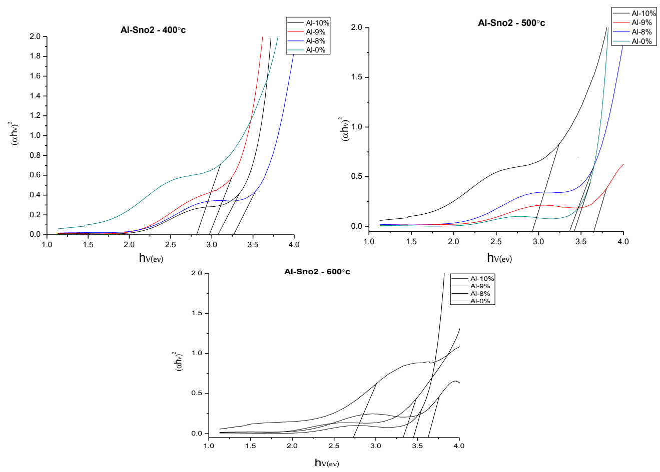

Fig. 4 Optical band gap of undoped and Al doped SnO_2 films deposited on glass substrates annealing at 400 °C, 500 °C and 600 °C

3.3 Scanning Electron Microscopic Study

The microstructures of samples are analyzed by scanning electron microscopy Instrument JSM – 6360 in Fig. 5. All the samples consist of many kinds of Al - SnO_2 microstructures with shapes that resemble tetrapods and some nanoparticles as well as an especially large number of small grains. However there are more Al - SnO_2 nanoparticles are small grains in higher concentration and higher annealing temperature is shown in Fig. 6. There might be an obvious advantage in using this material for gas sensors.

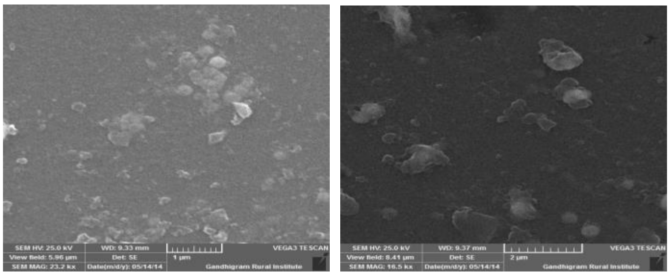

Fig. 5 SEM of a) undoped b) Al doped SnO_2 films deposited on glass substrates at 400 °C

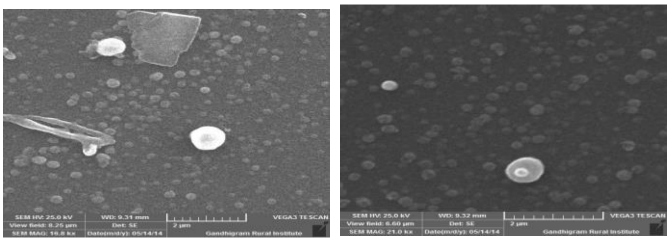

Fig. 6 SEM of Al doped SnO_2 films deposited on glass substrates annealing at 500 °C and 600 °C

The elemental composition obtained from the EDAX spectrum Fig. 7. The peaks show the element that has been detected from the sample confirming the presence of Al, Sn and Oxygen in Al - SnO_2 thin films.

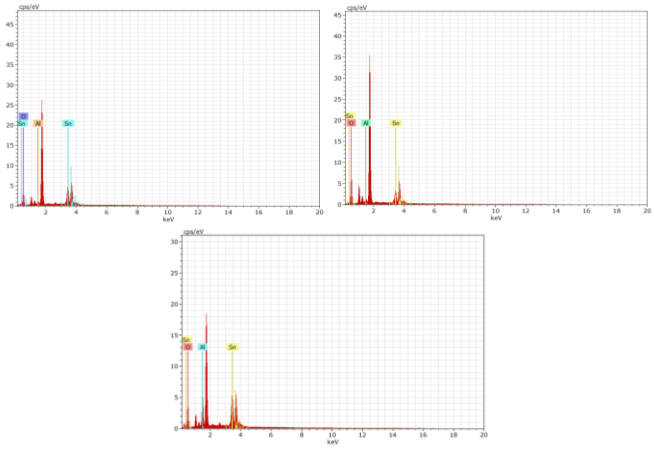

Fig. 7 EDAX of Al doped SnO_2 films deposited on glass substrates at 400 °C, 500 °C and 600 °C

4. Conclusion

Nanostructures of aluminium doped tin oxide thin films were deposited onto glass substrate using simplified low coast homemade spray pyrolysis technique with various aluminium concentration (8%, 9%, 10%) and annealing at 500 °C and 600 °C. The effect of Al concentration and Annealing to influence the changes of physical properties in Al: SnO_2 thin films, The X-ray diffraction patterns confirmed the proper phase formation of material and EDAX studies of the films showed that the exact amount of Al in the films are less that taken in the solution. SEM studies showed that the particle structure and size. Optical transmittance spectra of the films showed considerable high transparency 85%. In the visible region and the transparency decreases with the increase of Al doping and annealing effect in the films. The direct allowed band gap of the films have been found to lie with the range of 2.6 ev to 3.6 ev. More interesting the particle size, band gap decreasing with increasing Al concentration and annealing temperature. High electrical conductivity and high carrier concentration that we obtained are quite promising for gas sensing devices.

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