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Aluminium Doped Tin Oxide (ATO) Thin Films Grown onto Glass Substrate by Spray Pyrolysis Technique

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ABSTRACT

Nanostructured Al doped Tin Oxide (ATO) thin films were deposited on cleaned glass substrate by spray pyrolysis technique at 400 °C using a solution consisting of $SnCl_4$ starting as material and doping source $AlCl_3$ which were dissolved in methanol and stirred four hours. The effect of changes in doping source content of Al:SnO_2 thin films were investigated and studied the crystalline structure, surface morphology, transmittance and optical band gap of ATO films. The dopant concentration varied from 0 to 10%. X ray diffraction studies conformed the proper phase formation in the films are polycrystalline without any second phase with preferential orientations along the (110), (200), and (211) planes and an average grain size of 20 nm. The visible transmittance exceeds 85% and the optical band gap was estimated to be around 2.6 eV to 3.6 eV. The scanning electron microscopic (SEM) studies showed the particle size lying in the range 20 nm for undoped films and it is decreasing while increasing of Al doping.

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] and heat mirror for energy efficient windows [10]. For these applications many transparent conducting oxide TCO films were used such as SnO_2, ZnO, TiO_2 and In_2O_3 which should 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, 13]. 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+} 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. 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 [20] is 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 spray technique is the most suitable when high visible transmission and high infrared reflectance are desired.

2. Experimental Methods

Aluminium doped SnO_2 films were deposited onto the glass by spray pyrolysis technique. The starting material for Sn and doping source was aluminium chloride. Both precursor and doping compound were dissolved in ethanol. The starting doping ratio (Al/Sn) was 0% 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. After synthesizing the films, their structural, optical and electrical characterizations were performed.

The structural properties of the 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 synthesized and annealed Al-SnO_2 films were measured using a Shimadzu UV – 3101PC double beam spectrometer. The samples surface morphology was analyzed by the scanning electron microscopic.

3. Results and Discussion

3.1 X-Ray Studies

Fig. 1 showed X-ray pattern of sprayed undoped (SnO_2) and doped (Al - SnO_2) at 400 °C as prepared temperature. This spectrum 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 Scherrer formula [20], $D=0.94\lambda/\beta\cos\theta$, 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 strong (110 and (200) peaks. It was observed that the peaks base was broadened. It should confirm the nanostructures occurrence of the Al-SnO_2 sample. This was in well agreement with the SEM images. Fig. 2 shows that Al doping content to reduce the grain size. The effect of Al doping on SnO_2 has been investigated by various researchers in the past [19, 20]. With increasing Al dopant in the tin oxide film, the crystalline of SnO_2 decreased. Hence the doping element Al is a grain growth inhibitor.

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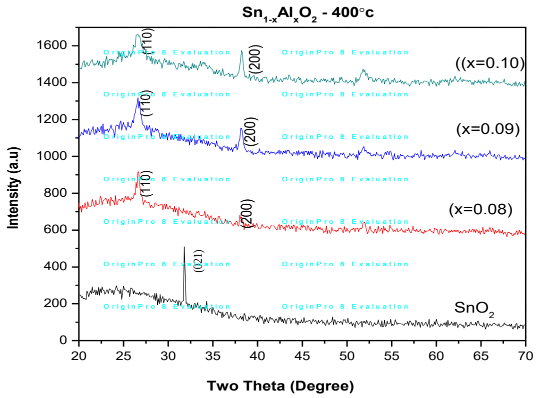

Fig. 1 XRD pattern of undoped and Al doped SnO_2 films deposited on glass substrates at 400 °C

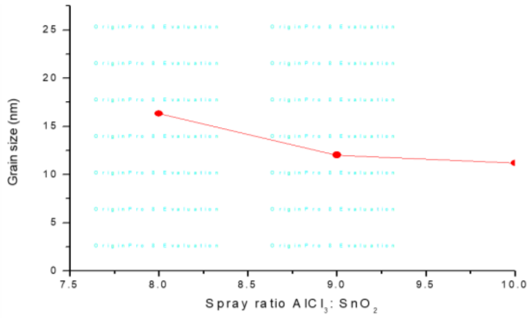

Fig. 2 Variation of grain size with doping ratio at 400 °C

3.2 UV-Visible Spectral Study

Al doped SnO_2 thin film optical constants of the different atomic percentage are measured using UV transmission spectrum Fig. 3 which shows transmission of Al doped SnO_2 thin films with Al concentration (0% to 10%) and temperature 400 °C (prepared). From the Fig. 3, it is observed that the transmission of the film decreases with increase in Al concentration. The average percentage of transmission of all the thin film samples is lies in 85% in visible region.

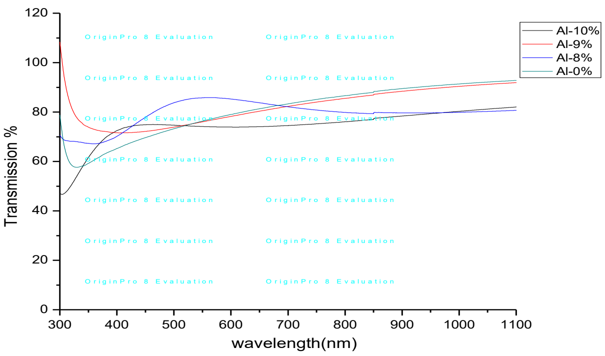

Fig. 3 Transmission spectrums of undoped and Al doped SnO_2 films deposited on glass substrates at 400 °C

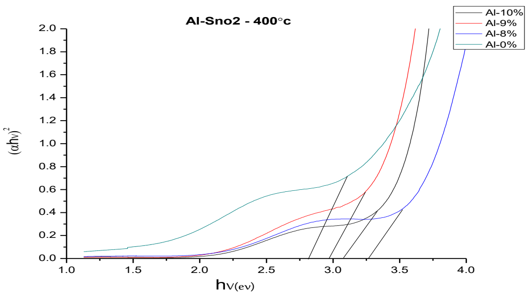

Fig. 4 Optical band gap of undoped and Al doped SnO_2 films deposited on glass substrates at 400 °C

The optical band gap of the deposited Al-SnO_2 thin films are calculated [20]. Optical band gap is determined by extrapolating of the linear part of the curve $(\alpha h\nu)^2$ vs $h\nu$ which intercepts the energy axis $h\nu$. From Fig. 4, it is observed the variation of band gaps due to the change in concentration of precursor solution and annealing temperature. The calculated band gap for 0% to 10% aluminium content at deposition temperature 400 °C is in the range of 3.62 eV to 2.63 eV for Al doped and un doped SnO_2 respectively. The band gap narrows down due to the decrease in the number of charge carriers with increasing in Al concentration.

3.3 Scanning Electron Microscopic Study

The microstructures of samples are analyzed by Scanning electron microscopy Instrument JSM – 6360 which is shown in Fig. 5. The samples consist some nanoparticles as well as an especially large number of small grains. However there are more Al-SnO_2 nanoparticles found as small grains in higher concentration. There might be an advantage while using this material for gas sensors.

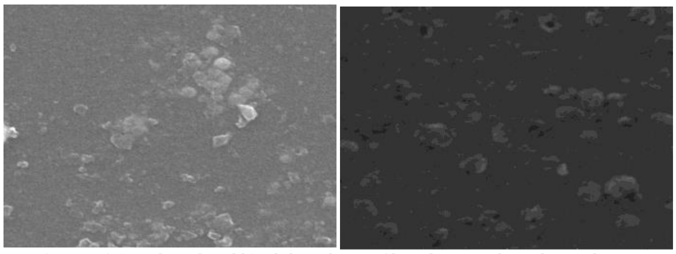

Fig. 5 SEM of a) undoped and b) Al doped SnO_2 films deposited on glass substrate at 400 °C

4. Conclusion

Nanostructures of aluminium doped tin oxide thin films were deposited onto glass substrate using simplified low cost spray pyrolysis technique with various of aluminium concentrations. The effect of Al concentration influence the changes of physical properties in Al:SnO_2 thin films. The X-ray diffraction patterns confirmed the proper phase formation of material. SEM studies showed that the particle structure and size. Optical transmittance spectra of the films showed considerable high transparency 85%. In the visible region, the transparency decreases with the increase of Al doping 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 interestingly, the particle size, band gap are decreasing with increasing Al concentration. Its high electrical conductivity and high carrier concentration that obtained from this work are quite promising for gas sensing devices.

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