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The Influence of Al and Zn Co-Doping on Optical and Structural Properties of Transparent and Conducting SnO_2 Thin Films Prepared by Spray Pyrolysis Technique

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ABSTRACT

The effect of Al and Zn Co-doping on the structural, electrical and optical properties of SnO_2 thin films have been studied. The undoped and aluminium and zinc co-doped SnO_2 nano crystalline thin films were prepared on glass substrates at 400 °C by spray pyrolysis technique. The starting material is ($SnCl_4.5H_2O$) and doping source are aluminium chloride and zinc chloride for tin (Sn), aluminium (Al) and zinc (Zn) respectively. The source materials have been dissolved in ethanol and stirred for four hours at 50 °C. The doping stoichiometric ratio was 4%. 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 film, Al and Zn Co-doped SnO_2 thin films have been characterized by different methods such as XRD, FESEM, UV-Vis NIR and EDAX analyses. The obtained results suggested that the prepared nanocrystalline thin films are suitable for gas sensor applications.

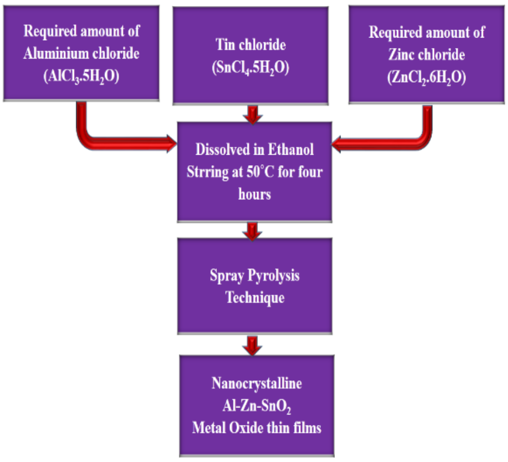
1. Introduction

Tin oxide (SnO_2) is being widely used in many fields owing to its good optical and electrical properties. In general, it is a non-stoichiometric prototypical transparent conducting oxide material. It has good adsorptive properties and chemical stability. It can be deposited onto glass ceramics, oxides and substrate materials [1, 2]. It has a high melting point and good transmission and does not easily react with oxygen and water vapor in the air, so it has a high specific volume and good cycling performance. Gas sensors based on SnO_2 thin films are used to detect a variety of hazardous gases, combustible gases, industrial emissions and pollution gases [3]. In addition, SnO_2 thin films are also used for transparent electrodes in display devices like LCDs and as transparent active layers in SnO_2 / silicon solarcells [4], thin film resistors, antireflection coatings, photochemical devices and electrically conductive glass [5]. The undoped tin oxide is a wide band gap semiconductor (E_g~ 3.6 eV) with electrical resistivity varying from 10 to 10^6 Ωcm^{-1}, depending on the temperature and stoichiometry of the oxide [1]. In the form of thin film it is a transparent material, characterized by high optical transmission in the visible range (~ 85%) [6]. Thin films can be prepared by a variety of methods such as chemical Vapor deposition (CVD), sputtering, so-gel process and spray pyrolysis. In compared with other deposition techniques, spray pyrolysis is the most attractive technique for industrial development due to its high deposition rate, competitive costs, good reproducibility and possibility of using commercially available large area deposition. The corresponding doped materials were respectively named AlO and ZnO. The properties of AlO and ZnO films make them very attractive for various gases sensors devices.

The doped and undoped SnO_2 nano crystalline thin film prepared by spray pyrolysis technique. Al and Zn doping has attracted the attention of many researchers since it has several advantage in terms of conductivity and chemical stability [7,8]. In the present study, we report on the deposition and characterization of Al-Zn Co-doped SnO_2 thin films prepared by spray pyrolysis technique. The aim of this work is to give an insight on how the deposition conditions including the deposition rate, the composition influence on the structural, optical and electrical properties of the produced films. Therefore a set of complementary investigation methods has been used to characterize the thin films.

2. Experimental Methods

Al-Zn-SnO_2 thin films were deposited by SPD technique. In this deposition technique a starting solution containing Al, Zn and Sn precursors was sprayed by means of nozzle assisted by a carrier gas, over a hot substrate. The starting solution and doping material was dissolved in ethanol and stirred four hours at 50 °C. The starting stoichiometry concentration of undoped SnO_2 and Al, Zn doped SnO_2 solution was 4%. The glass substrate was mounted on hot plate then heated to 400 °C. This was controlled by dimmarstat and digital thermometer connected to hot plate. Spray rate and substrate to nozzle distance were maintained at 10 mL/min and 25cm respectively. The schematic representation of experimental procedure is shown in preparation flow chart (Scheme 1) and Table 1.



Scheme 1 Preparation chart of Al-Zn Codoped SnO_2 Nanocrystalline Metal oxide thin films

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Table 1 The various process parameters in the Al-Zn-SnO_2 nanocrystalline thin films deposition

Precursors	$SnCl_4.5H_2O + AlCl_3.\ 5H_2O +\ ZnCl_2.\ 6H_2O$
Deposition rate	10 mL/min
Substrate temperature (°C)	400 °C
Nozzle to substrate distance	25 cm
Carrier gas pressure	30 Pa

A structural analysis has been carried out using X-ray diffraction (XRD). The crystalline structure was analyzed by X-ray diffraction using a diffractometer model DMA X2200 with the copper anticathode (CUKα, λ=1.5 Å) with an angle range 2θ of 20° - 70°. The surface morphology of the films and the cross section film thickness were obtained by using Field emission scanning electron microscope (FESEM) and also the chemical compositions have been determined using EDAX. The optical characteristics (transmittance and reflectance) have been evaluated in UV-Vis-NIR spectral range. The optical properties were measured by UV-Vis spectroscopy (shimaDZU UV-3101PC) double beam spectrometer.

3. Results and Discussion

3.1 Structural and Morphological Characterization of Al-Zn Doped SnO_2 Thin Films

Fig. 1 shows the XRD pattern of pure and Al, Zn Co-doped SnO_2 films with ratio of 4% deposited at 400 °C on glass substrates. The position of the diffraction peaks in the diffractogram was indexed and the corresponding values of interplanar spacing 'd' values were compared with the standard JCPDS values [9]. The observed X- ray diffraction peaks are corresponding to (110) and (021) planes. The mean crystallite size was calculated for the (110) plane diffraction peak by using the Scherrer's formula [10]

$$D = k\lambda / \beta\cos\theta$$

where β is the observed full width at half maximum, λ is the X- ray wavelength (0.1548 nm to CUKα) θ is the Braggs angle [11, 12]. Estimating d from the premium two XRD patterns, it has been detected that the mean particle thickness of the prepared and doped and doped films is about 38.2 nm and 27.3 nm respectively. The observed values are agreement with the reported values [13]. Hence aluminum, zinc co-doped tin oxide thin films is to be suitable for gas sensors.

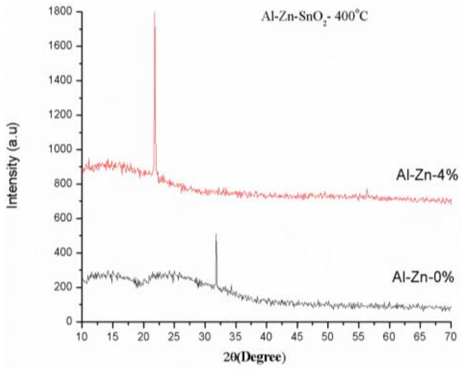

Fig. 1 XRD pattern of undoped and Al-Zn doped SnO_2 films deposited on glass substrate at 400 °C

Fig. 2a and b show surface morphologies of undoped and Al-Zn-SnO_2 thin films at 400 °C for concentration at 4%. It was quite clear that the surface nature of the films was greatly influenced by doping concentration. The surface morphology showed a closely packed arrangement of crystallites in both kinds of doped films. The particle size was observed slightly to be decreased with respect to the Co-doping and it can be clearly seen in the SEM images and also which were consistent with the XRD results.

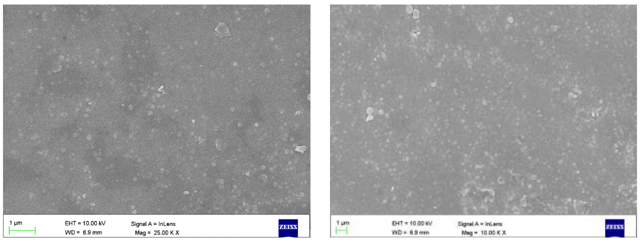

Fig. 2 a) FESEM of undoped SnO_2 thin films deposited on glass substrates at 400 °C; b) FESEM of 4% Al doped SnO_2 films deposited on glass substrates at 400 °C

3.2 Optical Properties of Al-Zn-SnO_2 Thin Films

Fig. 3 shows the optical transmittance spectra of the pure SnO_2 and Al, Zn Co-doped SnO_2 thin films in the wavelength range of 300 – 800 nm. In this figure, transmittance spectra showed sharp absorption edge in the wavelength region about 480 nm. The average transmissions of undoped and Al-Zn doped SnO_2 thin films showed higher transmittance in the visible region [14].

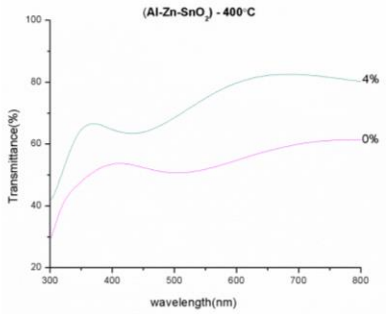

Fig. 3 Transmission spectra of undoped and Al-Zn co-doped SnO_2 thin films deposited on glass substrates at 400 °C

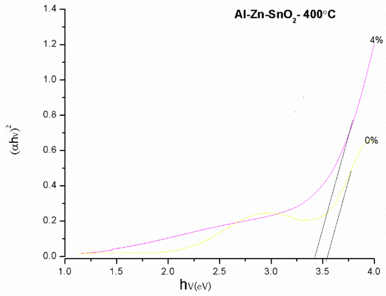

Fig. 4 Optical band gap of undoped and Al-Zn doped SnO_2 films deposited on glass substrates at 400 °C

Fig. 4 shows the direct optical band gap for undoped and doped thin films. The fundamental absorption which corresponds to electron excitation from the valence band to the conduction band gap. For the samples (αhv) curves correspond to the case of a crystalline material with direct allowed transmittance (direct gap) according to the following equation.

$$(\alpha h\nu) = (h\nu\text{-}E_g)^{1/2}$$

where α is the absorption coefficient, h is Planck's constant, v is the photon frequency Eg (eV) and A^* is a constant depending on the material and the direct optical band gap (Eg). From the plot optical gap is found to be 3.52 eV (for undoped) and 3.47 eV. There is a good agreement with literature values. This values varied depending on the dopants and preparation method.

EDAX spectrum of Al-Zn-SnO_2 is shown in (Fig. 5). The micrographs show high crystallinity of samples because of development of grains with well-defined boundaries. The EDAX spectrum confirmed the stoichiometric of all the elements in the samples in accordance with the theoretical calculations.

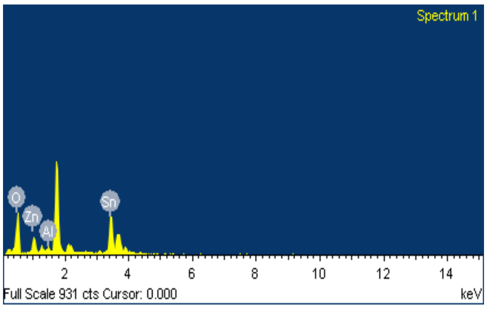

Fig. 5 EADX Al-Zn doped SnO_2 films deposited on glass substrates at 400 °C

4. Conclusion

The highly oriented nanocrystalline of Al-Zn Co-doped thin films was fabricated on to glass substrates at 400 °C by spray pyrolysis technique. The film structure, morphology and optical properties analyzed. It was found that the Nano crystalline SnO_2 grains possess the tetragonal rutile structure. The crystallite size of the films calculated from XRD depending

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on the kind of dopants. Transmission measurements performed on the synthesized films confirmed that they are highly transparent in the visible region. The band gap energy values was found to be 3.5eV and 3.2eV for undoped and Al-Zn Co-doped SnO_2 thin films respectively. The structure, morphology and optical properties of the films have been investigated. It has been found that the Co-dopant ratio is much effective on the structure, morphology and optical properties of the films. The investigation results of the Al-Zn-SnO_2 thin films prepared by Spray pyrolysis technique ensured their stability and suitability for gas sensor devices.

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