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Study of Structural, Electrical, Optical properties of Al and Zn Co-doped SnO₂ thin films Prepared by Spray Pyrolysis

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Abstract : The effect of doping SnO₂ thin films with Al and Zn concentration on the structural electrical optical properties of the films was studied. The undoped SnO₂ thin films and Aluminium and Zinc Co-doped SnO₂ thin films were prepared on glass substrates at 400°C by spray Pyrolysis technique. The starting material was (SnCl₄.5H₂O) and doping source was Aluminium Chloride and Zinc Chloride were used as a source for tin (Sn), Aluminium (Al) and Zinc (Zn) respectively. The source are dissolved in methanol and stirred at four hours in 50°C. The starting doping stoichiometric ratio of 0.04. The resulting solution was sprayed on glass substrate to nozzle distance were maintained respectively at 10ml/min and 25cm. the prepared samples to studied for effect of Al, Zn doped SnO₂ films on structural and optical properties of layers characterized by different method such as XRD, SEM, UV-Visible and EDAX. Their results show that the films have Nano-scale structure and it is suitable for gas sensors applications.

Keywords.. Al, Zn, SnO₂, Nanostructure, thin film, spray pyrolysis, physical properties

Introduction

Tin Oxide (SnO₂) is to be widely used in many fields owing to its good optical and electrical properties. It is naturally non-stoichiometric prototypical transparent conducting oxide. Because of it is good adsorptive properties and chemical stability. It can be deposited onto glass ceramics, oxides and substrate materials of other type². 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 SnO₂ thin films are used to detect a variety of hazardous gases, combustible gases, industrial emissions and pollution gases³. In addition SnO₂ thin films are also used for transparent electrodes in display devices like LCDs and as transparent active layers in SnO₂ / silicon solar cells⁴, thin film resistors, antireflection coatings, photochemical devices and electrically conductive glass⁵. The undoped tin oxide is a wide band gap semiconductor (E_g ~ 3.6 eV) with electrical resistivity varying from 10 to 10⁶ Ω cm, depending on the temperature and stoichiometry of the oxide¹. In the form of thin films is a transparent material, characterized by high optical transmission in the visible range (~ 85%)⁶. 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. This type of thin film 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.

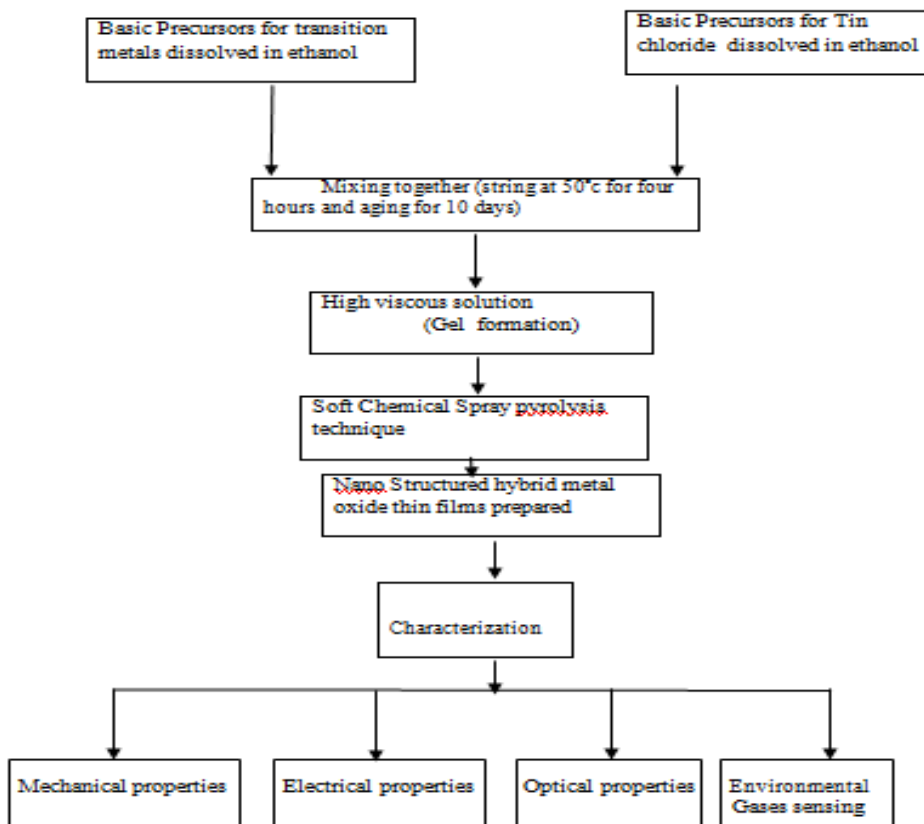
The doped and undoped SnO₂ thin film prepared by spray pyrolysis technique. For a single doped Al, Zn doping has attracted most of researcher's attention as it has several advantage in terms of conductivity and chemical stability^{7, 8}. In the present study we report on the deposition and the characterization of Al-Zn doped SnO₂ thin films obtained by spray pyrolysis technique. The aim of this work is to give an insight on how the deposition conditions influence the deposition rate, the composition, the structure and the optical and electrical properties of the produced films. Therefore a set of complementary investigation methods has been used to

characterize the thin films. A structural analysis has been carried out using X-ray diffraction (XRD). The optical characteristics (transmittance and reflectance) have been evaluated in UV-Vis-IR spectral range. The scanning electron microscopy (SEM) have been used to study the surface morphology and chemical compositions have been determined using EDAX.

Experimental

Al-Zn-SnO₂ 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 SnO₂ and Al,Zn doped SnO₂ solution was 4%. The glass substrate was mounted on hot plate then heated to 400°C. Which was controlled by dimmastrate and digital thermometer connected to hot plate. Spray rate and substrate to nozzle distance were maintained respectively at 10ml/min and 25cm. The schematic representation of experimental procedure is shown in flow chart.

Flow Chart Showing the Preparation of Al-Zn-SnO₂ Nano structure Metal Oxide Thin Films:



The crystalline structure was analyzed by X-ray diffraction using a diffractometer model DMA X2200 with the copper anticathode (CuK α , $\lambda=1.5\text{\AA}$) with an angle range 2θ of $20^\circ - 70^\circ$. The surface morphology of the films and the cross section film thickness were obtained by using scanning electron microscope (SEM-JSM 6360). The optical properties were measured by UV-Vis spectroscopy (Shimadzu UV-3101PC) double beam spectrometer.

Results and discussion

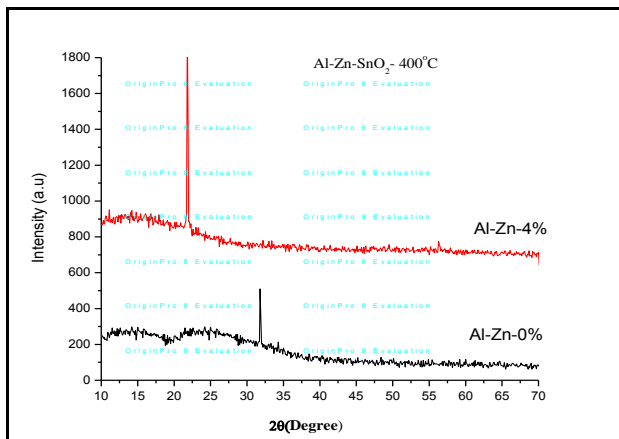
Structural and morphological characterization of Al,Zn doped SnO₂ thin films

(Figure 1) shows the XRD patterns of pure and Al,Zn doped SnO₂ films with ratio of 4% deposited at 400°C on glass substrates. The position of the diffraction peaks in the diffractogram were indexed and the corresponding values of interplanar spacing d were calculated and compared with the standard JCPDS values. The XRD reveals that for the crystal structure, X-ray diffraction peaks to (110) and (021) for undoped

SnO_2 thin films reveal reflection from the (110) planes. The mean crystallite size was calculated for the (110) plane diffraction peak by using the scherrer formula¹⁰

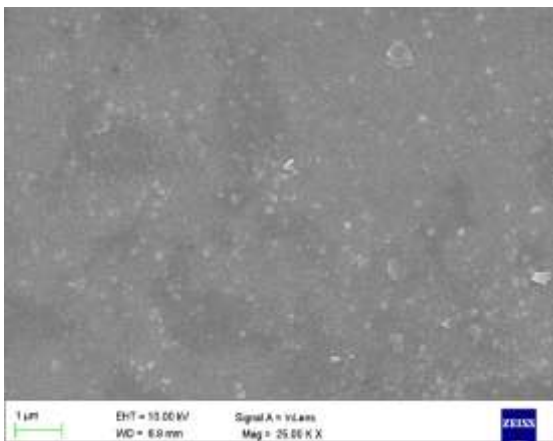
$$D = k\lambda / \beta \cos\theta$$

Where β is the observed angular width at half maximum intensity which is equal to $0.9 \cdot \lambda$ is the ray wavelength (0.1548nm to $\text{CuK}\alpha$) 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 38.2nm and 27.3nm respectively. The observed values is agreement with the reported values¹³. Hence Aluminum, Zinc Co doped Tin oxide thin films is to be suitable for gases sensors.

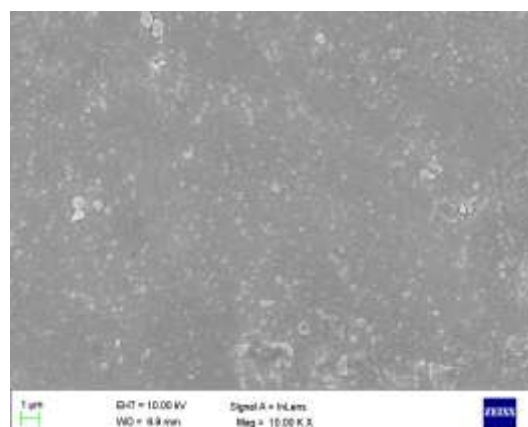


(Figure1) – XRD pattern of undoped and Al-Zn doped SnO_2 films deposited on glass substrates at 400°C

(Figure2a,2b) shows 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 doped films. The grain size slightly decreased was undoped and doped SnO_2 thin films. It decreased was clearly seen in the micrographs, which were consistent with the XRD analyses.



(Figure2b)



(Figure3b)

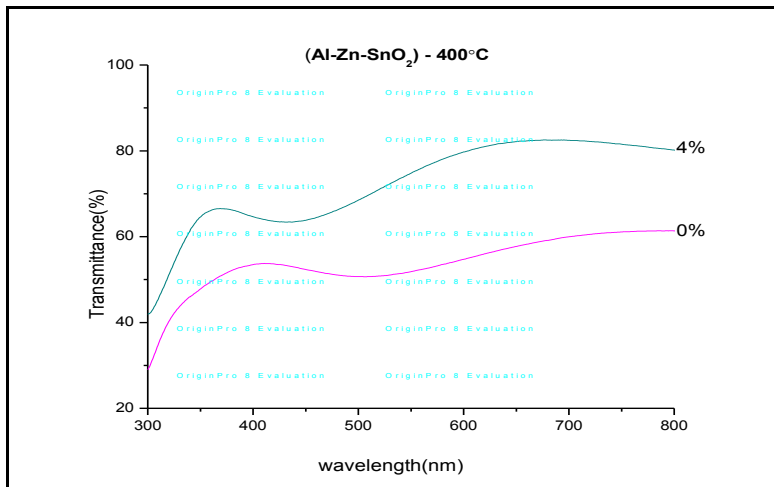
(Figure2b)- SEM of undoped SnO_2 thin films deposited on glass substrates at 400°C

(Figure3b) – SEM of 4% Al doped SnO_2 films deposited on glass substrates at 400°C

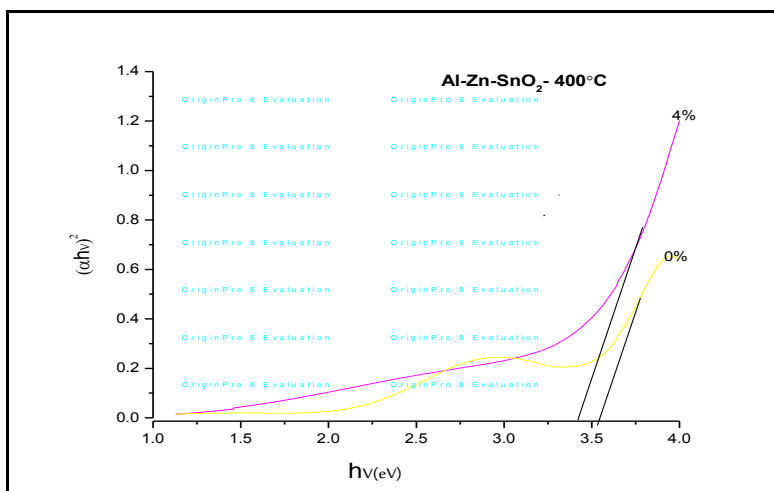
Optical properties of Al-Zn- SnO_2 thin films

(Figure3) shows optical transmittance spectra of the pure SnO_2 and Al, Zn doped SnO_2 thin films in the wavelength range of 300 – 800nm. In this figure, transmittance spectra showed sharp absorption edge in the

wavelength region about 480nm. The average transmissions of undoped and Al-Zn doped SnO₂ thin films showed higher transmittance in the visible region¹⁴.



(Figure3) – Transmission spectrums of undoped and Al-Zn doped SnO₂ films deposited on glass substrates at 400°C

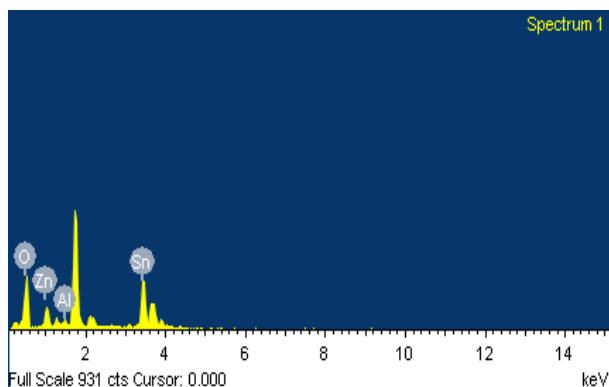


(Figure4) – Optical band gap of undoped and Al-Zn doped SnO₂ films deposited on glass substrates at 400°C

(Figure4) shows determined 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.

$$(\alpha hv) = (hv - E_g)^{1/2}$$

Where α (m^{-1}) is the absorption coefficient, $h(J.S)$ is Planck's constant, $\nu(HZ)$ is the photon frequency E_g (eV) and A^* is a constant depending on the material and the direct optical band gap (E_g). From the plot optical gap is found to undoped 3.52eV and 3.47eV. There is a good agreement with literature values. This values varied depending on the dopants and preparation method. EDAX spectra of AL-Zn-SnO₂ have been shown in (Figure5). The micrographs show high crystallinity of samples because of development of grains with well-defined boundaries. The EDAX spectra confirmed the stoichiometric of all the elements in the samples in accordance with the theoretical calculations.



(Figure 5) – EADX Al-Zn doped SnO₂ films deposited on glass substrates at 400°C

Conclusions

The high oriented crystalline of Al-Zn 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 SnO₂ grains possess structure of the tetragonal rutile structure. The crystallite size of the films calculated from XRD depending on the kind of dopant atoms. Transmission measurements performed on the synthesized films confirmed that they are highly transparent in the visible region. The band gap energy values was found 3.5eV and #.2eV for undoped and Al-Zn doped SnO₂ 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-SnO₂ thin films prepared by Spray pyrolysis technique ensure their stability and suitability for gas sensor devices.

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