Synthesis, Characterization and gas sensing performance of Al and Zn Co-doped SnO_2thin films Prepared by Spray Pyrolysis

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Abstract

In this work Al-Zn-SnO_2 thin films were deposited onto glass substrates at 400ºC byspray Pyrolysis technique. The films were studied the effect of dopingconcentration on the structural electrical optical properties of the Al-Zn-SnO_2films was studied. The undopedSnO_2 thin films and Aluminium and Zinc Co-doped SnO_2thinfilms were prepared.The starting material was ($SnCl_4.5H_2O$) 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 50ºC. 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 SnO_2 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: Nanostructure,thin film, spray pyrolysis, physical properties, Gas sensor

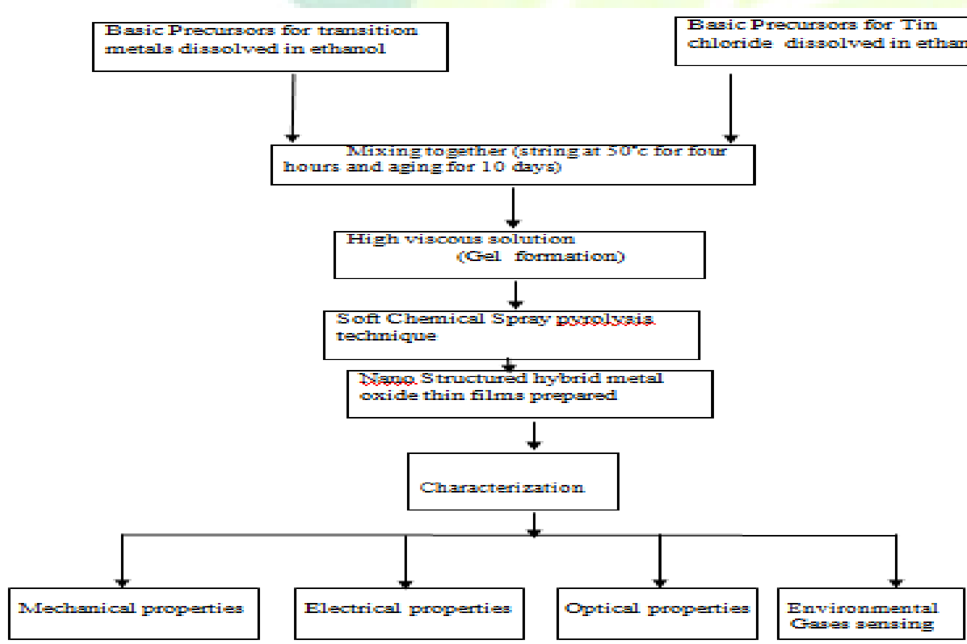
Introduction:

Tin Oxide (SnO_2) 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 type(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 (Eg 3.6eV) with electrical resistivity varying from 10 to 10^6 Ω cm, depending on the temperature and stoichiometry of the oxide(1). In the form of thin films is a transparent material, characterized by high optical transmission in the visible rang(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 SnO_2thin 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 SnO_2 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 structureand 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-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 50ºC. 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 400ºC. 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-SnO_2 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 (CUKα, λ=1.5Å) with an angle range 2θ of 20º - 70º. 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 SnO_2 thin films:

Fig(1) shows the XRD patterns of pure and Al,Zn doped SnO_2 films with ratio of 4% deposited at 400ºC 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(9).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 formula(10)

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

Where β is the observed angular width at half maximum intensity which is equal to 0.9. λ is the ray wavelength (0.1548nm 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 38.2nm and 27.3nm respectively. The observed values is agreement with the reported values(13). Hence Aluminum, Zinc Co doped Tin oxide thin films is to be suitable for gases sensors.

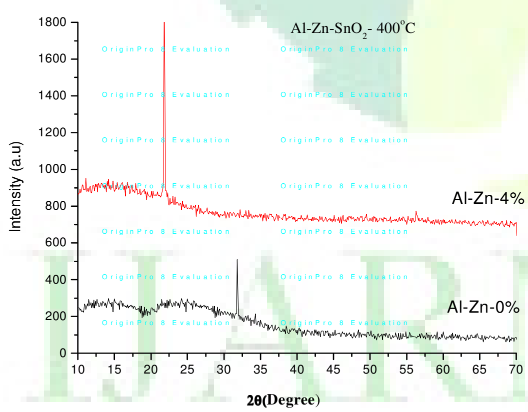
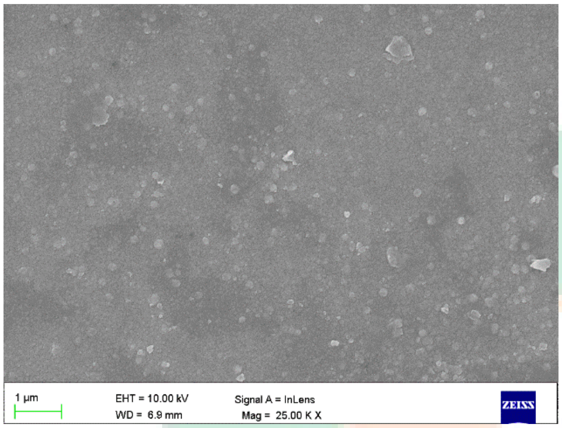


Fig. (1) – XRD pattern of undoped and Al-Zn doped SnO_2 films deposited on glass substrates at 400ºC

Fig(2a,2b) shows surface morphologies of undoped and Al,Zn-SnO_2 thin films at 400ºC 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.



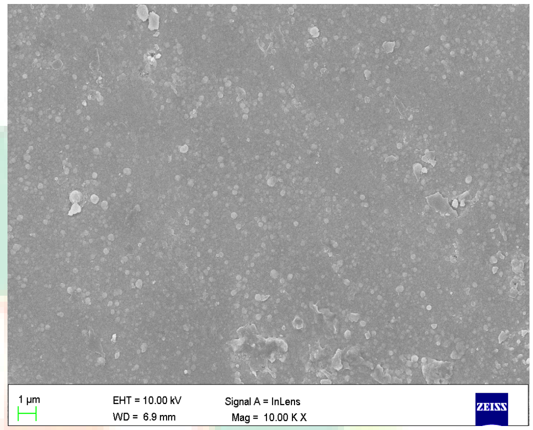


Fig. (2b)- SEM of undoped SnO_2 thin films deposited on glass substrates at 400°C

Fig. (3b) – SEM of 4% Al doped SnO_2 films deposited on glass substrates at 400°C

Optical properties of Al-Zn-SnO_2 thin films:

Fig(3) 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 SnO_2 thin films showed higher transmittance in the visible region(14).

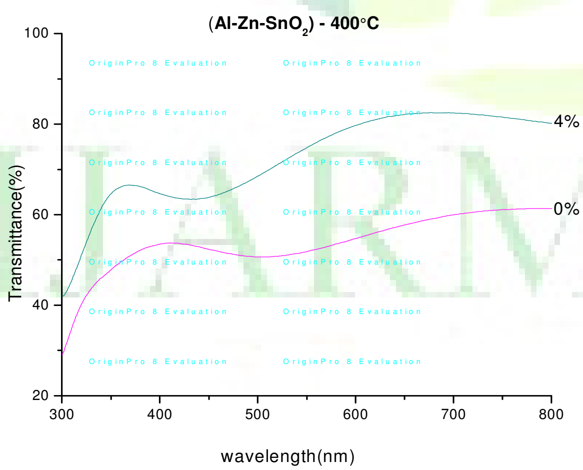


Fig. (3) – Transmission spectrums of undoped and Al-Zn doped SnO_2 films deposited on glass substrates at 400°C

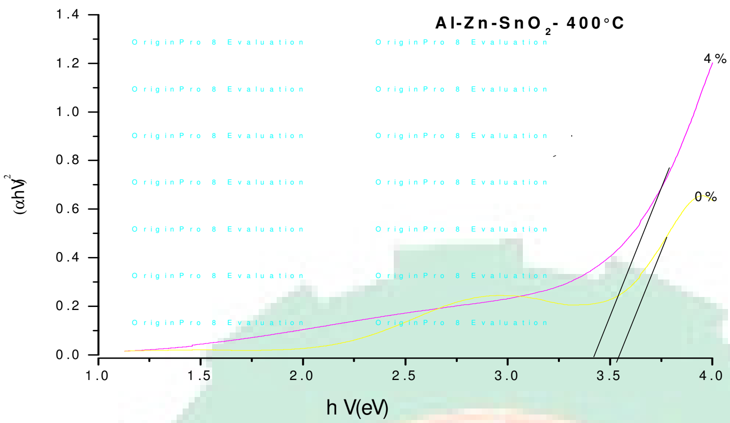


Fig. (4) – Optical band gap of undoped and Al-Zn doped SnO_2 films deposited on glass substrates at 400°C

Fig(4) shows 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 (αh□) curves correspond to the case of a crystalline material with direct allowed transmittance (direct gap) according to the following equation.

$(\alpha h\square) = (h\square\text{-}Eg)^{1/2}$

Where α (m^{-1}) is the absorption coefficient, h(J.S) is Planck's constant, □(HZ) 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 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-SnO_2have been shown in Fig(5). 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.

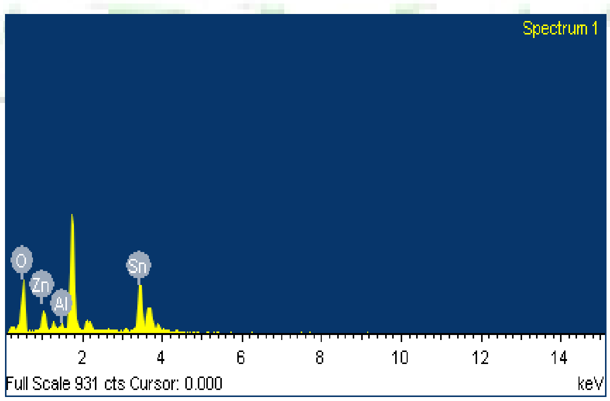
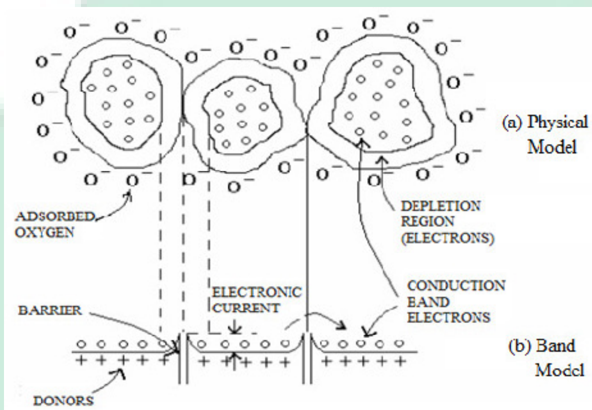


Fig. (6) – EADX Al-Zn doped SnO_2films deposited on glass substrates at 400°C

Gas sensing properties of Al-Zn-SnO_2 thin films:

The basicgas sensing properties of the Al-Zn- SnO_2 sensors were studied in a test chamber that allows the heating of their substrate. Additionally the sensors were evaluated for their response in dry air and humid air. For the measurement of electrical properties, the current-voltage (*I-V*) characteristics were measured by using high-voltage source/measure unit and the basic gas sensing characteristics of the Al-Zn- SnO_2 thin films were investigated as a function of operating temperature and test gas concentration. In the present studies the films were characterized by various parameter such as sensitivity, selectivity and response.



Energy band at grain boundary for SnO2

The sensitivity is defined as S= $(R_a-R_g)/R_g$, where R_g is the resistance in presence of test gas and Ra the film resistance in dry air, measured at respective decreases on gas exposure and vice versa.

The selectivity of a sensor towards an analyzing gas is expressed in terms of dimension that compares the concentration of the corresponding interfering gas that produce the same sensor signal. This factor is obtained by

Selectivity = (sensitivity of sensor for interfering gas)/ (sensitivity towards desired gas)

The response of time is the interval over which resistance attains a fixed percentage of final value when the sensor is exposed time is indicative of a good sensor.

Conclusions: The high oriented crystalline of Al-Zn doped thin films was fabricated on to glass substrates at 400ºC by spray pyrolysis technique. The film structure, morphology and optical properties analyzed. It was found that the Nano crystalline SnO_2grains 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 dopedSnO_2films 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_2thin films prepared by Spray pyrolysis technique ensure their stability and suitability for gas sensor devices.

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