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Nanocrystalline pervoskyte $ZnSnO_3$ thin films for detection of H_2 gas

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Abstract : Pervoskyte nanocrystalline $ZnSnO_3$ thin films were prepared by spray pyrolysis technique. Nonocrystalline $ZnSnO_3$ thin films were characterized by different analytical technique exhibits X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. Prepared sensor showed a better sensitivity (S ~ 91) at operating temperature of 300 °C for 500 ppm to H_2 gas with the short response (5 sec.) and quick recovery times (13 sec.), respectively. The results are discussed and interpreted.
Keywords: Spray pyrolysis techniques, nanocrystalline pervoskyte $ZnSnO_3$, H_2 sensor, sensitivity

1. Introduction

Growing industrialization and ever increasing pollutants from vehicular exhaust have resulted into increased air pollution. The problems related to air quality monitoring are important issues of the current research activity. In fact, a key component in many process controls, product development, environmental monitoring etc. is the measurement of concentration of one or the other gaseous component of the ambient. In such situations suitable sensors can provide the necessary interface between the ambient and the back up electronic instrumentation to detect the target gas [1, 2].Gas sensors based on metal oxide semiconductors may be used in a wide variety of applications including gas monitoring and alarm applications [3].

$ZnSnO_3$ (Zinc stannate) material has recently attracted much attention due to its controversial basic material properties, [4] such as its fundamental band gap. The interests in pervoskyte type oxides are mainly due to the easy modification of their electric properties by the selection of an adequate atom A or B [5, 6]. The data on the synthesis of $ZnSnO_3$ are ambiguous and contradictory and among the large studies of materials, the details on ternary oxide systems with spinel or pervoskyte structure have been rarely published [7].

Hydrogen can be mainly used for energy generations in the near future due to the fact that fuel cell electricity generators are clean, quiet and more efficient than any other known technology. It is therefore straightforward that in all these applications safety measures are of highest concern due to the explosive properties of hydrogen [8].

The deposition of nanocrystalline pervoskite $ZnSnO_3$ using spray pyrolysis techniques is advantageous as it can produce highly crystalline and stratified structures. This is an important feature since high crystallinity and having layered formation can allow for greater sensitivity [9].

In this paper, the authors report about the response of nanocrystalline pervoskite $ZnSnO_3$ thin films to various gases. It emerges that the film exhibit good response to gases at the temperature range of 200–400 ^oC. In this work, spray pyrolysis technique has been used for the deposition of nanocrystalline pervoskite $ZnSnO_3$.

Samples were characterized using X-ray diffractogram (XRD) and field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). Electrical conductivity was measured using gas sensing system.

2. Experimental

2.1. Preparation of nanocrystalline pervoskite $ZnSnO_3$ thin films

Nanocrystalline pervoskite $ZnSnO_3$ films were prepared on preheated glass substrate using a spray pyrolysis technique and the experimental set up is described elsewhere [9]. The 0.05 M Zinc chloride ($ZnCl_4 \cdot 5H_2O$ Purified Loba Chemie) and Stannic chloride ($SnCl_4 \cdot 5H_2O$ 99.9% pure, Aldrich Chemie) were prepared in deionized water. For spray combustion with volume ratio of Zn and Sn is (4:6) sprayed the solution for different interval of time 10 min, 20 min, and 30 min, respectively. The optimized values of preparative parameters are: spray rate (9 ml/min), distance between substrate to nozzle (30 cm), to and fro frequency (14 cycle). Each solution was filled in a spray gun and was allowed to spray on heated glass substrate at constant temperature 400 ^{0}C. Thus the thin films with different spray deposition time were obtained and referred as S1, S2 and S3. These thin films were annealed at 500 ^{0}C in a muffle furnace for one hour in an air medium.

Table 1. Process parameters for the spray deposition of pervoskite $ZnSnO_3$ thin films are shown in Table 1.

Name of the Sample	Volume ratio of Zn / Sn		Spray deposition time (min.)	Substrate temperature (^{0}C)	Annealing temperature (^{0}C)
S1	4	6	10	400	500
S2			20		
S3			30		

3 Materials Characterization

3.1 Thickness measurement

The film thickness of the as-deposited films was measured by a well-known a weight difference method [10]. In order to measure the thickness of the thin films by using weight difference method, error and accuracy was found to be ± 5 % nm. The thickness, sample weight and sample area are related as:

$t = M/A.\rho$ ---------- (1)

Where, M is the weight of the sample in gm,

A the area of the sample in cm^2

and ρ the materials density in gm cm^{-3}.

The values of the film thickness were found to be 223 nm to 330 nm respectively.

3.2. Structural studies

The X-ray diffraction patterns were recorded from 20 to 80^o as shown in Fig. 1. The phase purity of the film was analyzed with X-ray diffractogram (Miniflex Model, Rigaku, Japan) using CuKα radiation with a wavelength of 1.542 Å. The diffraction peaks from various planes (100), (063), (028), (085) and (024) are matching well with standard ASTM data for pervoskite $ZnSnO_3$.

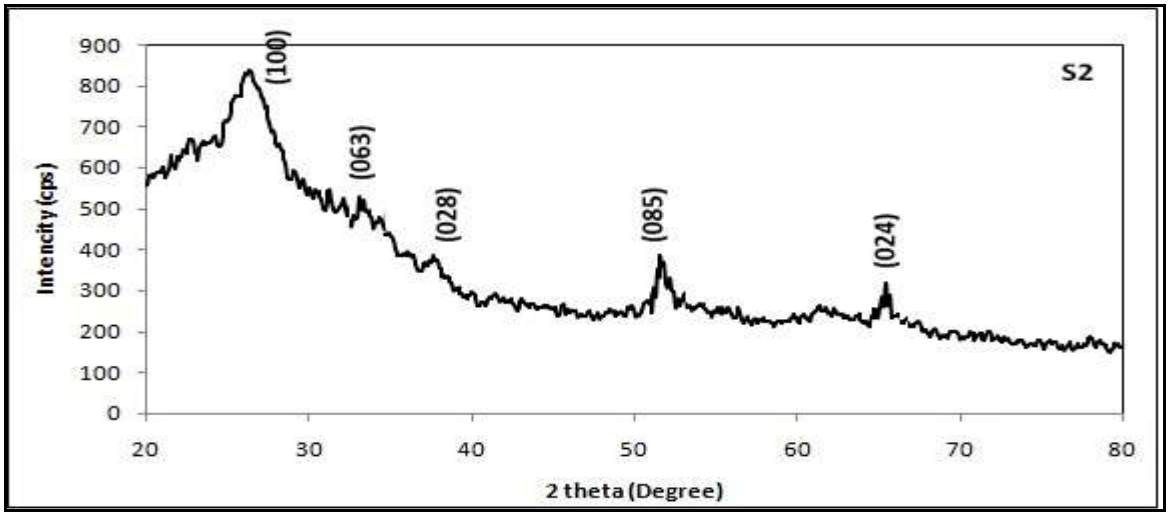


Fig 1: X-ray diffractogram of most sensitive nanocrystalline $ZnSnO_3$ thin film sample S2.

The information of the average crystallite size was obtained by Scherrer formula,

$D = 0.9\lambda/\beta\cos\theta$ ---------- (2)

Where, D = Average crystallite size

λ = X-ray wavelength (1·542 Å)

β = FWHM of the peak

θ= Diffraction peak position.

The average crystallite size was found to be 13 nm.

3.3. Surface morphology studies using FESEM and TEM

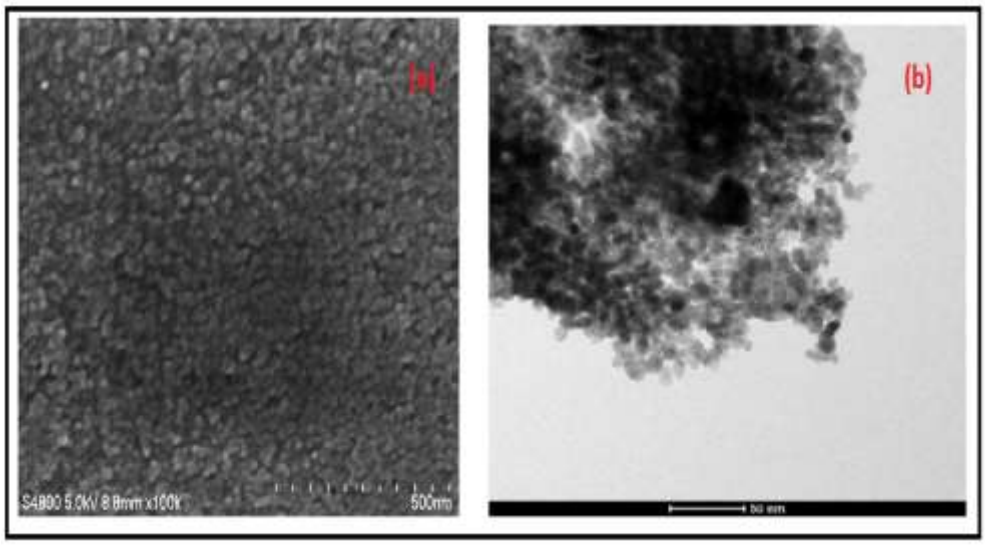


Fig. 2 (a) and (b): FE-SEM (a) and TEM (b) images of most sensitive sample S2

The surface morphology of the prepared film was analyzed using a field emission scanning electron microscope coupled with energy dispersive X-ray analysis (EDAX) (FE-SEM, JEOL. JED 6300). FE-SEM imaged of nanocrystalline $ZnSnO_3$ thin films were represented in Fig.2 (a). The average grain size was around 18 nm.

Microstructure property of nanostructured $ZnSnO_3$ thin films were obtained by using transmission electron microscopy (TEM) [CM 200 Philips (200 kV HT)]. Figure 2 (b) shows the TEM images of $ZnSnO_3$ thin films annealed at 500 ^{0}C. The grains are observed to nanocrystalline with spherical in shape. The crystallite size was found to be 16 nm.

3.4. Electrical properties

3.4.1. Measurement of I-V characteristics and Electrical conductivity

Fig.3 (a) depicts the I-V characteristics of the nanocrystalline $ZnSnO_3$ thin film. It is clear from the symmetrical I-V characteristics that the silver contacts on the film were ohmic in nature. Fig.3 (b) shows the variation of log (conductance) with temperature. The conductance values of all samples increase with operating temperature.

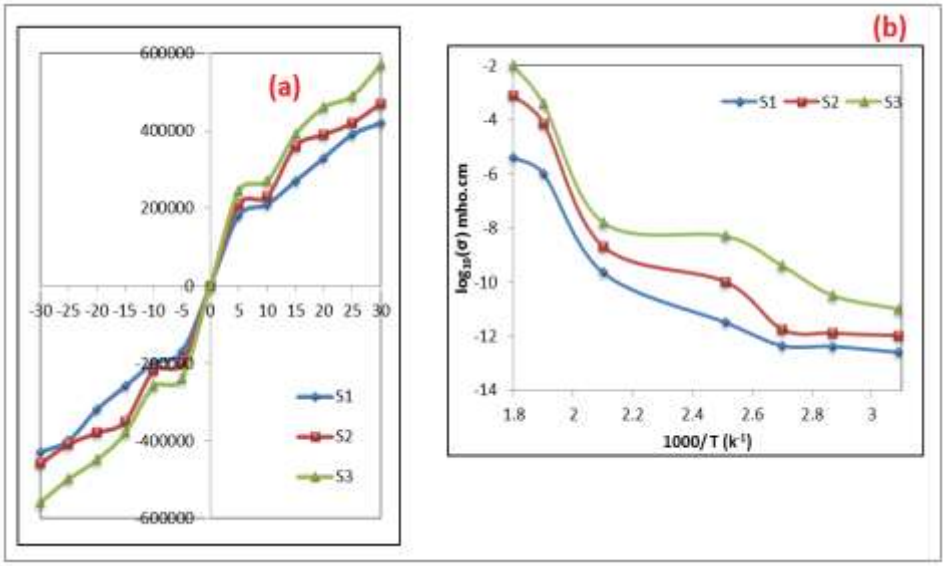


Fig. 3: Profile of I-V characteristics (a) and electrical conductivity (b)

They are nearly linear from 200 ^{0}C to 250 ^{0}C. The increase in conductance with increasing temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of the nanocrystalline $ZnSnO_3$ thin film [9].

4. Gas sensing performance of thin film

4.1 Details of Gas Sensing Unit

The sensing performance of the sensors was examined using a 'static gas sensing system', the details of gas sensing system was described elsewhere [10]. There were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage (10 V) was applied to the sensor, and the current was measured by a digital Pico ammeter. The air was allowed to pass into the glass chamber after every gas exposure cycle.

4.2 Sensitivity

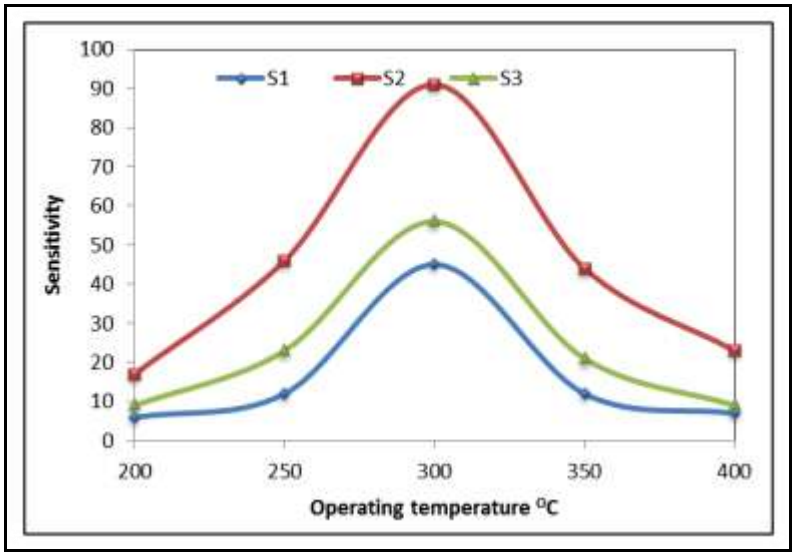
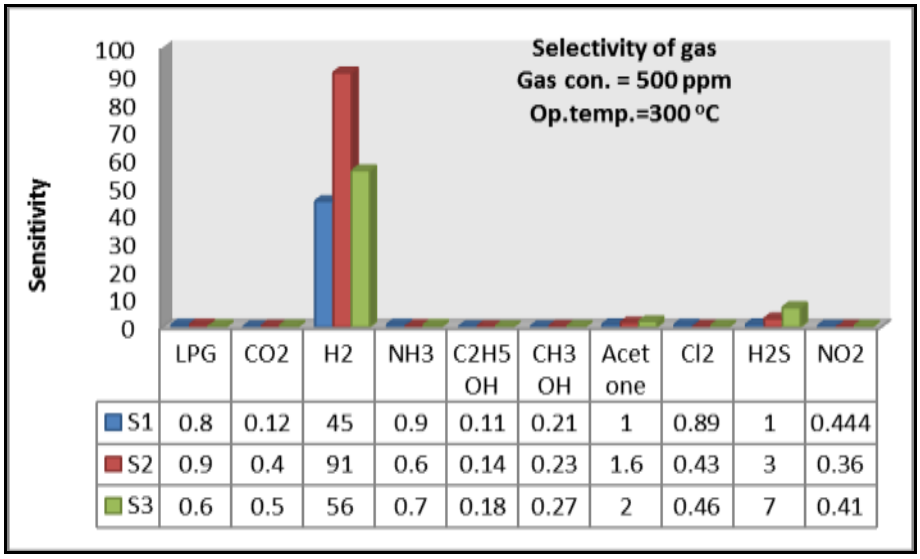


Fig. 4: Gas response with operating temperature

Fig. 4 shows the variation of sensitivity of nanocrystalline $ZnSnO_3$ thin film to H_2 gas (500 ppm) with operating temperature. The response was observed to increase with operating temperature up to 300 ^{0}C and then decrease with a further increase in operating temperature. The maximum gas sensitivity of nanocrystalline $ZnSnO_3$ thin film to H_2 (S=91) was acheived at 300 ^{0}C.

4.3 Selectivity



	LPG	CO2	H2	NH3	C2H5OH	CH3OH	Acetone	Cl2	H2S	NO2
S1	0.8	0.12	45	0.9	0.11	0.21	1	0.89	1	0.444
S2	0.9	0.4	91	0.6	0.14	0.23	1.6	0.43	3	0.36
S3	0.6	0.5	56	0.7	0.18	0.27	2	0.46	7	0.41

Fig. 5: Selectivity profile against various tested gases.

Fig. 5 depicts the selectivity of nanocrystalline $ZnSnO_3$ thin film sensor for H2 (500 ppm) gas at 300 ^{0}C. The sensor showed high selectivity for H_2 and could distinguish the H_2 among all the gases, such as LPG, CO2, H_2, NH3, C2H5OH, CH3OH, H_2S and Cl2.

4.4 Response and Recovery Time

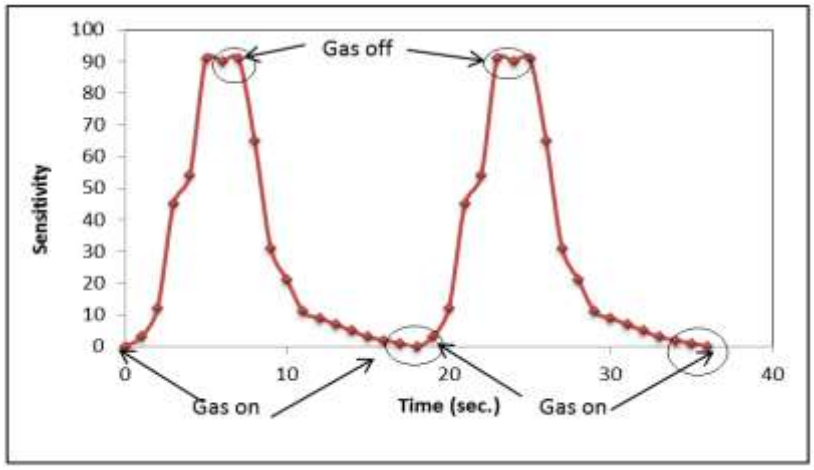


Fig. 6: Response and recovery profile of the sensor.

Fig. 6 shows the response and recovery characteristics of $ZnSnO_3$ thin film sensor to 500 ppm. The response of nanocrystalline $ZnSnO_3$ sensor was found to be quick (~ 5 s) to 50 ppm of H_2S, while the recovery was fast (~ 13 s). The fast response may be due to faster oxidation of the gas. The negligible quantity of the surface reaction product and its high volatility explains its fast response and quick recovery to its initial chemical status [11].

5. Gas sensing mechanism

Fig. 7 shows the H_2 sensing mechanism (Fig. (a) Before exposure of H_2 and (b) after exposure of H_2) of nanocrystalline $ZnSnO_3$ thin films. When the oxidation reaction rate of H_2 is much higher than the rates of adsorption and desorption of the reactants, the steady state oxygen coverage depends critically on the relative oxygen and H_2 concentrations in the gas phase [12]. Oxidation of H_2 on a tin oxide surface may occur through many different reaction paths, depending on the surface composition, structure and temperature and on adsorbed species. Most of the time, the intermediates and complexes formed during reaction are short-living compounds that are not easily identified. However, in order to understand the overall sensing mechanism of H_2, it is necessary to know what oxygen species are present on the surface and their extent, how does H_2 adsorb on the surface, which reaction paths are possible and which is the rate of each step, what other elements may interfere in the reaction and if they are present.

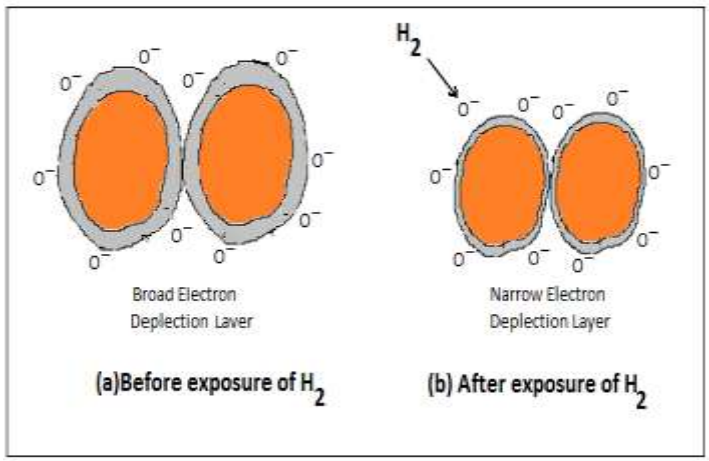


Fig 7: Sensing mechanism of $ZnSnO_3$ thin film

The response of the sensing materials is based on chemisorption, i.e. the exchange of charge between absorbed gases and the metal oxide surface [13]. In air, there are several different negatively charged oxygen

adsorbates, such as O_2^-, O^-, and O^{2-}, which are known to cover the metal oxide surface. The formation of an oxygen adsorbate layer leads to a decrease in the electron density on the metal oxide surface due to charge transfer from the metal oxide to the adsorbate layer. When the metal oxide used as a sensing material is exposed to reducing gas molecules, the gas molecules are oxidized by the oxygen ions on the metal oxide surface, resulting in the release of free electrons to the metal oxide and consequently, to an increase in the conductance (decrease of resistance) of the metal oxide [14].This implies that the gas sensing behavior of a metal oxide semiconductor is strongly related to its surface properties. Then, by varying the surface morphology, it is possible to tune the gas sensing properties of a material. Indeed, depending on surface properties of the nanocrystallites, a unique combination of structural, electronic, and adsorption/desorption process parameters can be obtained, thus the design of nanomaterials with controlled shape and/or morphology can participate to the enhancement of the sensing properties.

When they are operated in the semiconducting temperature range, the overall resistance of the sensor element is determined by the charge transfer process produced by surface reaction and by the transport mechanism from one electrode to the other through sensing layer, Therefore the microstructure of the sensing layer plays a key role for the development of an effective gas sensor .

6. Conclusions

1. Nanocrystalline perovskyte $ZnSnO_3$ thin films could be prepared by spray pyrolysis technique on heated glass substrate.
2. The structural investigation were carried out using XRD which reveals that formation of nanocrystalline perovskyte $ZnSnO_3$ thin films.
3. Surface morphology studies confirm that the as-prepared perovskyte $ZnSnO_3$ thin films were nanocrystalline in nature.
4. Gas sensing performance shows maximum gas response towards the H_2 gas.
5. Selectivity profiles chosen the H_2 gas against various tested gases.
6. Nanocrystalline perovskyte $ZnSnO_3$ thin film shows fast response and recovery time.

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