Ethanol-Sensing Characteristics of Tin Oxide (SnO_2) Nano-Particle Thin Films Deposited Using Ultrasonic Nebulizer

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Publication Info

Article history :

Received : 06th Sept., 2018

Accepted : 04th Dec., 2018

DOI : 10.18090/samriddhi.v10i02.10

Keywords : SnO_2, thin film, Spray pyrolysis technique, transmittance property, ethanol gas sensitivity.

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Abstract

Tin oxide (SnO_2) nano particle thin film has been deposited by spray pyrolysis technique using ultrasonic nebulizer of chloride solution ($SnCl_2.2H_2O$) over the glass substrate. An aqueous chloride solution was converted into a mist form of vapor using ultrasonic nebulizer and deposited over the heated substrate at temperature 300 ± 10^0C. The XRD and SEM result shows a regular, smooth, excellent morphology and also found polycrystalline in nature which is also evident in XRD analysis. The average grain size of SnO_2 particles were found to be in the range of 25 nm to 35 nm depending on the allowed concentration of chloride solution which is calculated from XRD plot using Debye - Sherror formula. The average thickness of the as prepared film was measured of the order of 120 nm. The optical transmittance properties of the SnO_2 thin films have been also measured. The films exhibited an average transmittance value of 93% in recorded range of wavelength. Finally the ethanol gas sensing properties of the thin film (0.1 M concentration) was performed and discussed in detail.

1. INTRODUCTION

In all over the world volatile organic compounds (VOCs), a serious concerned regarding to the environment with their speedy evaporation and foremost existence, are harmful due to its toxic nature for the human beings [1].Tin oxide (SnO_2) semiconducting film (n type semiconductor) intensively used in the field of stable gas sensors and microelectronics specifically in recognition of Volatile Organic Compounds (VOC's). At higher temperatures, applications of tin oxide (SnO_2) thin film is not only limited to the research laboratory but also used commercially in environmental monitoring, large scale industries, sophisticated electronic sensors etc. by using the sensitivity, selectivity and reliability properties of the film[2]. The excellent gas sensing properties of tin oxide thin films have been reported by different researchers for different gases like CO, NO_x, H_2S, H_2, CH_4, C_2H_5OH and CNG etc. [3-5]. The different techniques have been utilizes in preparation of a good SnO_2 thin films like thermal evaporation [6-7], chemical vapor deposition [8-9], RF magnetron co-sputtering [10-11], Sol gel[12], Electro deposition [13-14], laser pulse evaporation [15-16] and spray pyrolysis [17-20].

Among all the techniques spray pyrolysis has been used extensively due to its less expensiveness, large area deposition and chemically viable technique. It is reported by different workers that the grain size can be easily controlled at the atomic level i.e. working at solution level of SnO_2 thin film provides the better results [21-22]. It is also important to optimize the concentration of the starting material (i.e. solution) which highly affects the nature of the film mainly its grain size, growth of the film, gas sensing properties and optical characteristics [7,12]. The present study, focused on the optimization, is used for preparing good tin oxide thin film via spray pyrolysis using ultrasonic nebulizer.

We have investigated electrical, optical and ethanol gas sensing properties of the SnO_2 thin film prepared at 0.1M concentrations. XRD, SEM analysis was also performed for the structural, microstructural and surface morphology of the as prepared SnO_2 thin film deposited on the glass substrate. In this paper we also investigated the ethanol sensing characteristics of the as deposited SnO_2nano-particle thin film. We have found that the film exhibit selectively high response to ethanol at low operating temperatures and concentrations. To the best of our knowledge no such selective high response ethanol has been reported earlier in case of the sensing characteristics of the SnO_2 thin films grown by spray pyrolysis using ultrasonic nebuliser.

2. EXPERIMENTAL DETAILS

2.1 Preparation Method

SnO_2 thin film was successfully prepared by spray pyrolysis using ultrasonic nebulizer on glass substrate. Starting material for preparation is chloride solution of $SnCl_2$. $2H_2O$ of concentrations 0.1 M. The chloride solution was prepared by appropriately weighted and mixed in ionized water followed by steering of the solution of 3 hour subjected to the homogeneity of the solution. Prepared chloride solution was filtered and mixed with 1 ml methanol at every 5 ml of chloride solution. Methanol helps to decomposition of chloride solution and forms a SnO_2 film over heated substrate. The glass substrate was carefully cleaned with dilute HCl and gutted with acetone to remove the contamination if present over the surface of substrate. The substrate temperature and spray rate was maintained at 300 ± 10^0C and 1 ml/min respectively. Compressed and purified air was used as a carrier gas. After deposition, films were taken out from the heater surface by cooling it at room temperature. The various process parameters used in the film deposition are listed in Table -1

Table-1 : The various process parameters for the film deposition are listed in table-

S.No.	Spray Parameters	Optimised value
1	Deposition rate	1 ml/min
2	Substrate temperature	300±100C
3	Deposition time (in minute)	60 min
4	Nozzle to substrate distance	5 cm
5	Carrier gas	Compressed air
6	Solvent	Distilled water
7	Nozzle type	Glass (L shape)

2.2 Characterization of the SnO_2film

The prepared SnO_2 film was possess a grazing incident XRD measurement to analyzing the micro structural and structural study of film by using SIEMENS diffraktometer model-D5000, Scanning Electron Microscopy (SEM) also performed analysis of surface morphology by JEOL JSM model-5600. The optical transmittance spectra of the as deposited film were recorded in the wavelength range 340 nm to 995 nm using VIS-IR spectrophotometer SHIMADZU model -1601. Finally, gas sensing properties and electrical resistivity has been performed using Vander Pauw technique via four-probe method. The contacts of the four probes were made by silver and a gas sensing property was performed in a closed chamber of 1 liter capacity attached with temperature controller that control the temperature of the heater surface. Keithley sensitive digital voltmeter model - 182 and programmable current source model –224 used to determine the electrical resistivity of the prepared SnO_2 thin film.

3. RESULT AND DISCUSSION

3.1 Structural and Microstructural analysis of SnO_2 film

Structural analysis of the deposited SnO_2 film was carried out by using CuKá radiation, source having wavelength 1.5406 Å. XRD patterns of the film show well defined peaks having orientations in the planes. For comparing observed, calculated and standard interplanar spacing for SnO_2 Peaks, 05–0640 JCPDS card was referred. The standard interplanar spacing matches well with the calculated and observed value. To more precise, the value of full width at half maxima depends on the length over which the periodicity of the crystal is complete. The sharpness and strength of the peaks in 0.1M concentration appeared in SnO_2 thin film XRD plot as in fig.1. To obtain more quantitative information, the XRD pattern was analysed with Gaussian function where Full Width at Half Maxima [FWHM] was determined from the Debye-Sherror formula [10].

The crystalline grain size measurement was determined by the formula -

$$D = \frac{0.9\,\lambda}{\beta\ cos\theta}$$

Where, D = Crystalline grain size.

β = FWHM of the observed peak.

λ= wave length of the X-ray diffraction

θ = Angle of diffraction

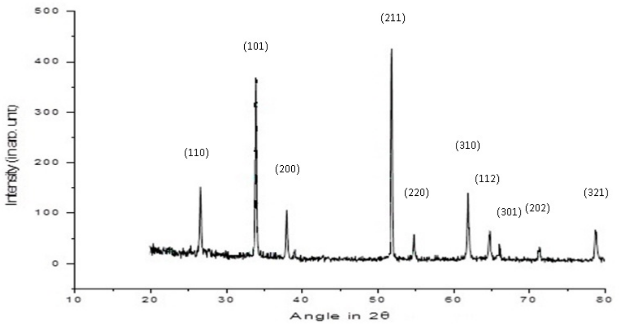

Fig.1: XRD pattern of as deposited nano-crystalline SnO_2 thin film

Using Scherrer-formula for peak (211) plane, average grain size of deposited film, calculated 0.25 nm to 0.35 nm. The observed results were comparable to the previous reported result [23]. The observed XRD peaks was analysed and shown in table 2.

Table-2 : X-ray diffraction analysis of SnO_2 thin film shown in table.

S.No.	Peaks (2θ)	Observed intensity	(hkl)	d spacing (Å)	FWHM	Grain size (in nm)
1	26.65	151	(110)	3.057	0.187	27.377
2	34.0	367	(101)	2.350	0.207	33.040
3	38.05	105	(200)	2.074	0.187	32.700
4	51.9	425	(211)	1.569	0.224	35.069
5	54.85	57	(220)	1.474	0.185	30.210
6	62.0	139	(310)	1.300	0.299	32.124
7	64.9	65	(112)	1.236	0.223	25.086
8	66.1	38	(301)	1.214	0.174	30.000
9	71.45	32	(202)	1.121	0.168	28.000
10	78.8	66	(321)	1.014	0.132	27.000

The SEM micrograph shows the surface topography of SnO_2 thin film of concentration 0.1 M as in fig.2. It is observed that the film of 0.1 M constriction has smooth surface morphology. The quantitative analysis of the film was carried out by energy dispersive spectroscopy and the spectrum obtained shown in a fig.3 (a) and (b). From the spectrum it is clear that only Sn and O are present in appropriate percentage 19 % and 81% respectively. The film show the polycrystalline in nature and uniform distribution of spherical grains relatively higher density which is in good agreement with already reported result [24].

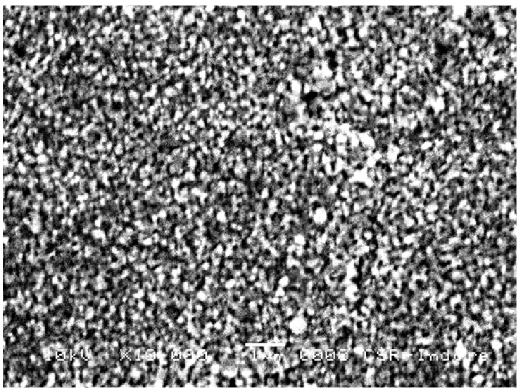

Fig.2: SEM microstructural structure of SnO_2 thin film showing uniformity in distribution of grains of size approximately 25nm to 35nm

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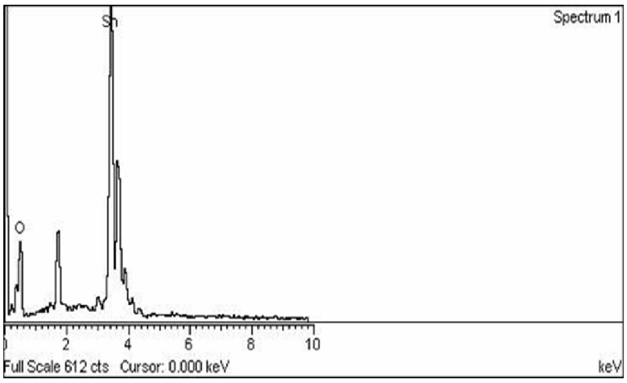

Fig.3(a): confirmative composition and material EDAX analysis of as deposited film i.e. SnO_2 thin film

Element	App	Intensity	Atomic%
	Conc.	Corrn.	
Sn L	2.13	0.9106	19.12
O K	0.53	0.3925	80.88
Totals			100

Fig.3(b): EDAX chemical analysis of as deposited film i.e. SnO_2 thin film.

3.2 Optical characterization of SnO_2 film

The optical transmittance spectra of the deposited film was observed. The optical transmittance (%T) of the film 0.1 M concentration with wavelength shown in a fig.4. The maximum transmittance 93 % has been observed for the film. The absorption coefficient can be calculated from the Lambert's formula [24].

$$\alpha = \left(\frac{1}{t}\right)\log\left(\frac{1}{T}\right)$$

Where,

t = thickness of the film and

T= transmittance of the film

Fig.5 shows the variation of $(\alpha h\nu)^2$ and $(h\nu)$ for the determining the band gap Eg of SnO_2 film by extrapolating of curve to $(h\nu)$ axis where the line meet to $(h\nu)$ axis gives the value of band gap (Eg). The incident photon energy is related to the direct band gap by following equation-

$$(\propto h\nu) \propto (h\nu - Eg)^{\frac{1}{2}}$$

Where, Eg is the optical band gap of the film

The calculated energy band gap for the as deposited film of 0.1 M is 3.42eV.

3.2 Gas (Ethanol) sensitivity of the SnO_2 film

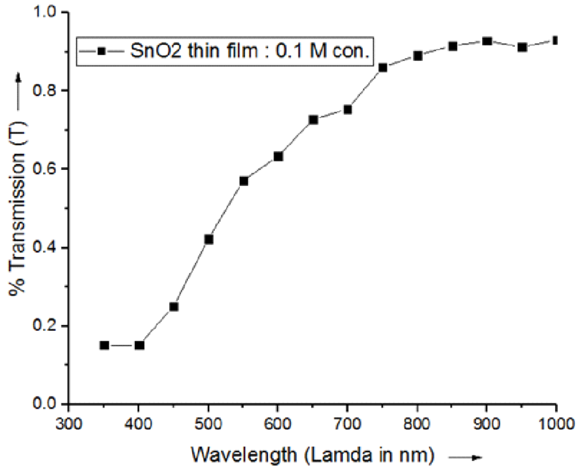

Fig. 4 : (%) Transmission spectra of SnO_2nano crystalline thin film

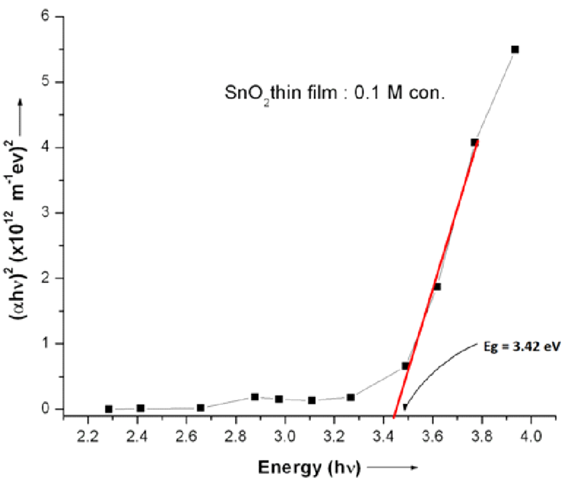

Fig.5: Graph of energy band gap of as deposited nano-crystalline SnO_2 thin film (Eg= 3.42 eV)

It has been observed that the film having less concentration shows a better sensitivity for ethanol gas. The sensitivity of the film is calculated by the change in the surface resistance in presence of gas i.e. the ratio of surface resistance of the film in air (Ra) and in gas (Rg) represents the sensitivity. As the temperature increase the sufficiently decrease in the surface resistance have been observed. The reasons of decease in resistance due to the ethanol vapor react with the chemisorbed oxygen and re-inject the carriers. This chemisorption with SnO_2 film exists for a limited temperature range. At sufficiently high temperature the surface of the oxide semiconductor an O_2^- or O^- liberate an electron from the conduction band of the n-type semiconductor. Due to lattice interaction of an electrons the surface resistance increased sufficiently as in fig.6. The effect of chemisorptions discussed in details by V. S. Vaishnav et al. [7]. The gas sensitivity of the as prepared SnO_2 thin film for ethanol gas also has been performed for 0.1 M concentration. The plot shown in fig.7 represents the variation in the sensitivity to the different range of temperature.

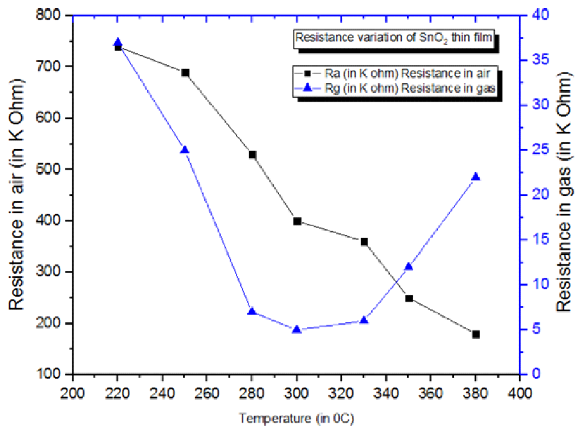

Fig.6: Resistance changes in air and ethanol atmosphere at 100 ppm of SnO_2 deposited film

Fig.8 shows the plot representing the variation of resistance with time to optimize the selectivity of the film SnO_2 thin film of 0.1 M concentration. The rapid decrease in resistance has been observed in the 170 sec. to 370 sec after injection of ethanol gas in chamber of 1 litre capacity. This result reveals that within 200 sec the resistance of the SnO_2 thin film decreases 270 Kohm forms its normal value.

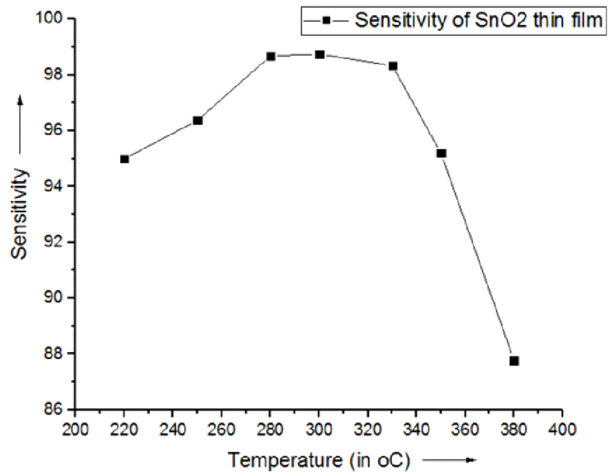

Fig.7 : Variation of ethanol gas sensitivity with temperature at 100 ppm photo luminescence

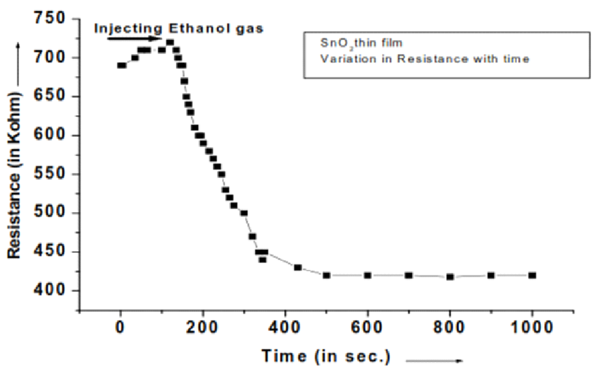

Fig.8 : Variation in resistance of SnO_2 thin film in ethanol atmosphere (100 ppm) with time

4. CONCLUSION

A formation of highly oriented SnO_2 nano crystalline thin film using aqueous chloride solution ($SnCl_2.2H_2O$) is confirmed. The structural, electrical, optical and gas (ethanol) sensing properties were studied. The sample exhibit rutile type crystal structure and preferred orientation along (211) plane for 0.1 M solution. Band gap

S-JPSET : Vol. 10, Issue 2, ISSN : 2229-7111 (Print) and ISSN : 2454-5767 (Online)

Eg of as deposited film is 3.42 eV with higher transmittance property. The substrate temperature and spray rate kept at 300 ^{0}C and 1 ml/min. are favourable conditions for the formation of a good quality SnO_2 nanocrystalline thin film. The quality of the film is comparable to the deposited through established aqueous route of SnO_2 deposition with different existing deposition methods.

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