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OPTICAL AND GAS SENSING CHARACTERISTICS OF TIN OXIDE NANO-CRYSTALLINE THIN FILM

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Transparent conducting tin oxide (SnO_2) thin film has been deposited on glass substrate by spray pyrolysis technique, taking starting material tin chloride solution ($SnCl_2.2H_2O$) and using ultrasonic nebulizer at substrate temperature 300±10 ^oC. The XRD result shows a regular, smooth morphology. The deposited film was found to be polycrystalline. The average grain size of SnO_2 was found to be 48.6 nm as calculated by XRD using Debye Scherrer Formula .After annealing the film in air at 400 ^oC the grain size was 51.02 nm. The thickness of the deposited film was of the order of 500 nm. The optical absorption, transmittance, reflectance and optical conductivity have been measured. It was found that the average transmittance of the film is around 78 % at wavelength 550 nm. Finally the ethanol gas sensing properties of the film was also performed.

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Keywords: SnO_2 thin film; Spray pyrolysis Technique; Surface morphology; Optical properties

1. Introduction

In the last decade, among the known oxide, tin oxide (SnO_2) semiconducting film has been intensively used in the field of microelectronics and stable gas sensors, specifically in recognition of volatile organic compound (VOC). The film is highly transparent, chemically inert, and mechanically hard. Application of the tin oxide films are not limitted to the research laboratory but are used commercially in environmental monitoring , industrial electronic sensor , liquid crystal displays etc [1].Owing to its low resistivity and high transmittance, tin oxide thin films are as a window layer in solar cells [2] . The gas sensing properties of tin oxide thin films have been performed for different gases like CO, NOx, H_2S, H_2, CH_4 and CNG etc. [3-5]. Doped or undoped tin oxide films can be deposited by several methods such as Thermal Evaporation [6-7], Chemical Vapor Deposition [8-9] R.F. Magnetron Co- sputtering [10-11], Laser Pulse Evaporation [12-13] and Spray Pyrolysis [14-15]. Among all technique spray pyrolysis has been used extensively beeing less expensive, large area deposition and chemically viable technique. It has been reported by different workers that the grain size can be easily controlled at the atomic level, and solution level [16-17]. Jagadish et al [18] studied the optical and electrical properties of spray deposited films . Concentration of the starting material (solution) highly affects the nature of the film mainly its grain size, growth of the film, gas sensing properties and optical characteristics [19,7]. The present analysis is focused on optimization, for depositing good tin oxide thin film by spray pyrolysis and to investigate structural, optical and gas sensing properties of SnO_2 thin film at molar concentration 0.1M.

2. Experimental details

2.1 Deposition Method of SnO_2 Thin Film:

SnO_2 thin film has been successfully deposited by spray pyrolysis. The film is deposited using tin chloride solution of concentration 0.1M mixed in tripled distilled water and 0.1ml methanol was added for every 5 ml of tin chloride solution .Methanol helps decomposition of chloride solution and forms a SnO_2 film on a heated substrate in air. The sprayed solution was deposited on the glass substrate that was carefully cleaned with dilute HCl and finally cleaned with acetone .The substrate temperature and spray rate was maintained at 300±10 ^oC and 0.5 ml/min respectively.

2.2 Characterization of SnO_2 Thin Film

The deposited SnO_2 film is characterized by XRD measurement using SIEMENS diffraktometer model-D5000. The optical transmittance spectra of the deposited films were recorded in the wavelength range of 340 nm to 995 nm using VIS-IR spectrophotometer SHIMADZU model -1601. Finally, gas sensing properties have been performed using Vander Pauw technique via four-probe method. The contacts of the four probes were made by silver past and gas sensing properties have been preformed in a closed chamber of 1 liter capacity attached with temperature controller that controls the temperature of the heater surface. The thickness of film was measured by Sloan Dektak 3D Surface Profilometer.

3. Result and discussion

3.1 Structural and Micro-structural analysis of SnO_2 Film:

Structural analysis of the deposited SnO_2 film was carried out by using CuKα radiation, source having wavelength 1.5406 Å. The X-ray diffraction pattern of the film is recorded. Figure. 1(a), 1(b) shows the XRD patterns of spray deposited undoped tin oxide thin film which is crystalline in nature with well defined peaks that match standard interplanar spacing JCPDS card no. 05–0640 and (hkl) values are shown in Table 1.

Table 1. (hkl) Value of XRD at 300 ^oC.

2θ	D value	hkl
26.8	3.460	110
31.06	3.325	101
33.99	2.884	200
38.05	2.637	111
52.08	2.4510	211
54.66	2.050	220
61.52	1.426	310

These Values were compared with the reported value [20]. The substrate temperature plays an important role in the film formation. When the substrate temperature is below 260 ^oC the spray falling on the substrate will under go in complete thermal decomposition giving foggy film whose transparency as well as electrical conductivity will be very poor. The substrate temperature is to high > 500 ^oC , the spray gets vaporized before reaching the substrate and the film becomes almost powder. Where the optimum substreat temperature in the range of 260 ^oC -500 ^oC the spray reaches the substrate surface in the semi-vapour state and complete oxidation takes place. To obtain more quantitative information, the XRD pattern was analyzed with Gaussian function where full width and half maxima [FWHM] was determined. The grain size of SnO_2 thin film D; can be estimated by the Debye-Scherrer formula [10].

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

Where, D = Crystalline grain size.
β = FWHM of the observed peak.
λ= wave length of the X-ray diffraction
θ = Angle of diffraction

Using Scherrer Formula the average grain size of deposited film, is calculated as 48.6 nm .It is also observed that if the undoped film deposited 300 ^{o}C was annealed in air at 400 ^{o}C , the number of peaks increased but at the same time there was a sharp increase in resistance which may be due to further oxidation and also grain size increases to 51.02 nm. Figure.1 (b) Compare the result [21]

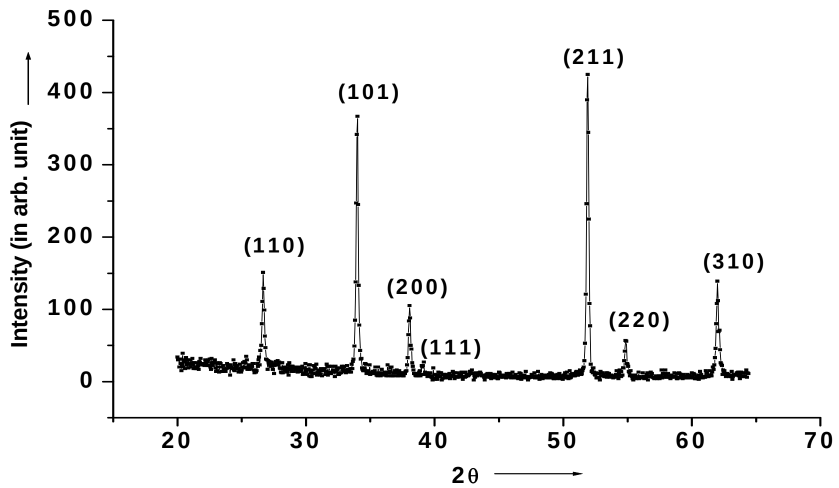

Fig.. 1(a) XRD of SnO_2 thin film deposited at temperature 300 ^{o}C

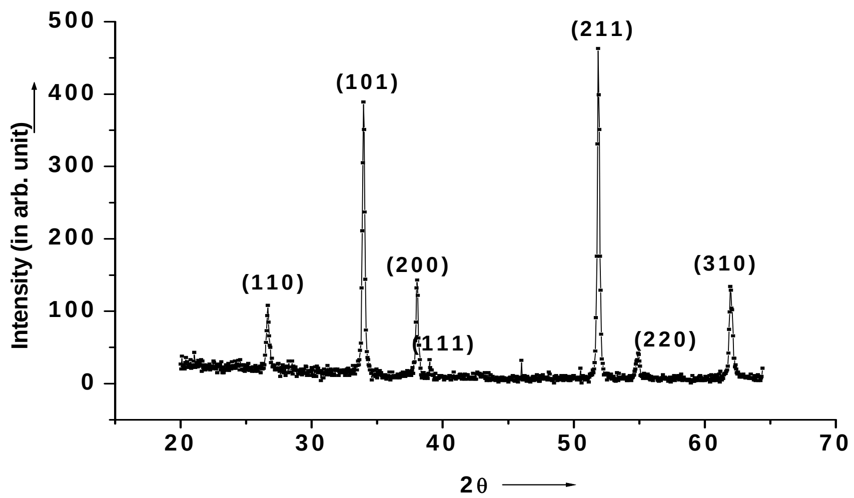

Fig. 1(b) XRD of SnO_2 thin film anneled at temperature 400 ^{o}C

3.2 Optical Characterization of SnO_2 Film

The optical transmittance spectra of the deposited film were recorded. The variation of optical transmittance (%T) with wavelength λ of 0.1M of the spray deposited tin oxide film at substrate temperature 300 °C .It was found that the average transmittance of the film is 78% Figure 2 . The absorption coefficient can be calculated from the Lambert's formula [22].

$$\alpha = (1/t) \log (1/T) \quad (2)$$

Where, t = is a thickness of the film
T= is a transmittance of the film.

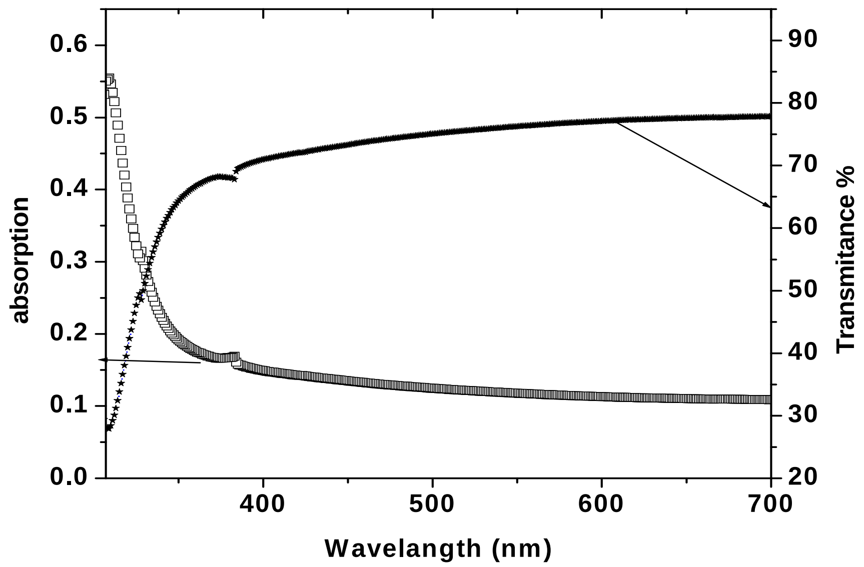

Fig.2. Absorption and Transmission Spectrum of SnO_2 thin film

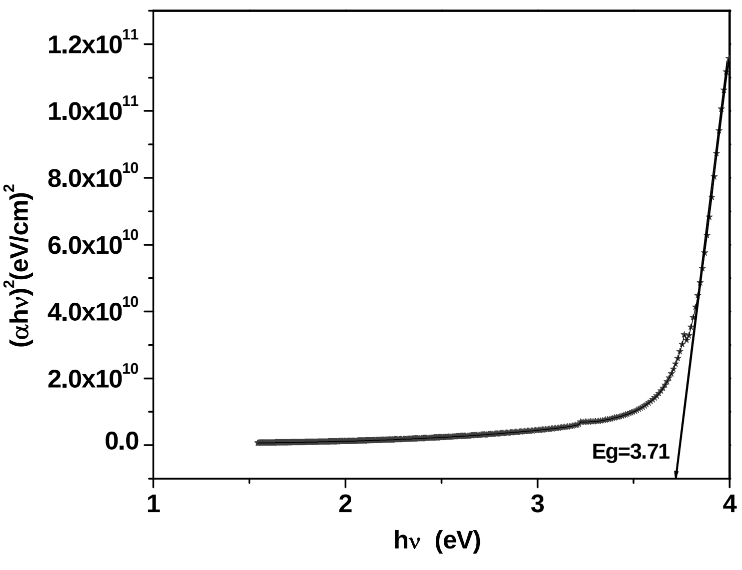

Fig. 3. Toue Plot of $(\alpha h\upsilon)^2$ with photon energy in SnO_2 thin film

Fig. 3 shows the variation of $(\alpha h\nu)^2$ & $(h\nu)$ for the determining the band gap Eg of SnO_2 film by extrapolation of curve . The incident photon energy is related to the direct band gap Eg by equation-

$$(\alpha h\nu) \ \alpha \ (h\nu - Eg)^{1\backslash 2} \quad (3)$$

The optical band gape was estimated in lower wave length region and it was found to be 3.71 eV. The reflectance (R) has been found by using relation ship

$$R+T+A=1$$

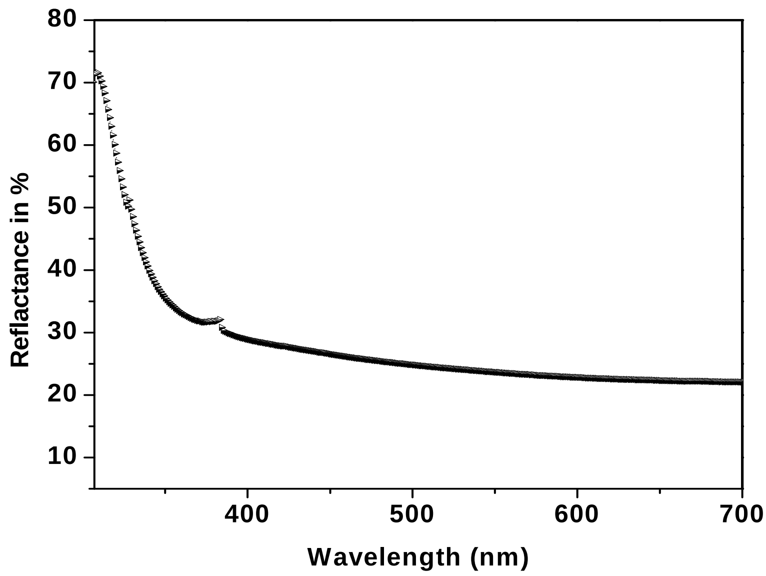

Fig. 4. Reflectance Spectra of SnO_2 thin film

As shown in Fig. 4.The refractive index (n) is calculated by the formula [23].

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (4)$$

The variation of optical conductivity (σ) with (hν) in Fig. 5 .The optical conductivity (σ) was determined using the formula

$$\sigma = \frac{\alpha n c}{4\pi} \quad (5)$$

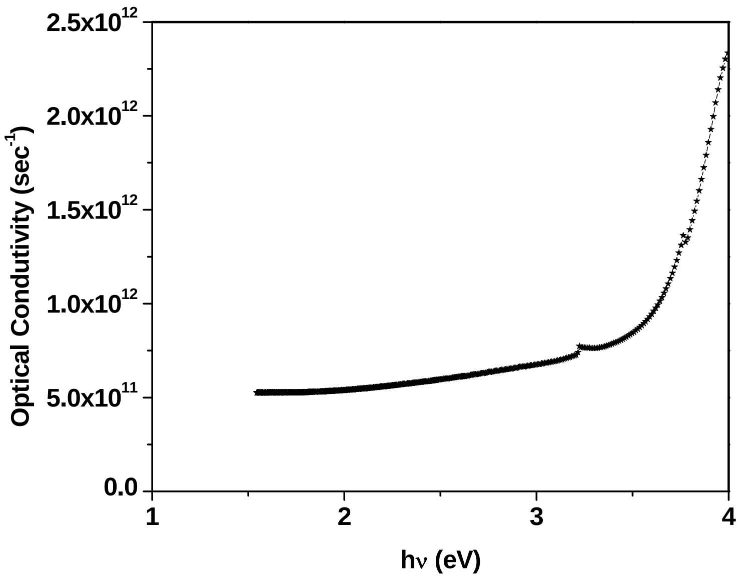

Fig.5. Change in opetical conductivity of SnO_2 thin film.

3.3 Gas (Ethanol) Sensitivity of the SnO_2 Film

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. It had been reported that gas sensing mechanism of most oxide semiconductor gas sensors was based on the absorption of gas on the surface [24]. The reason of decrease in resistance is because the surface of SnO_2 is covered with chemisorbed negative oxygen ion which could react with the β-H of C_2H_5OH and also found from differential thermal analysis (DTA) the endothermic weight loss due to sublimation and evaporation decrease the film resistance provide the optimum temperature range 260-380 ^oC , for sensitivity of SnO_2 thin film . When SnO_2 thin film is exposed to air , an oxygen ion molecule is absorbed onto the surface of SnO_2 sensor to form O_2^- or O^- , ion by attracting an electron from conduction band of the SnO_2 thin film as shown in equation, $O_2 + 2e = O_2^{2-}$ or $2O_2 + 1e = 2O_2^-$. So the high resistance of SnO_2 thin film is present in air. For active ethanol gas at moderate temperature, the ethanol gas reacts with oxygen ion molecule on the surface and gives up electron as can be described by,

$$2C_2H_5OH + O_2^{2-} = 2CH_3CHO + 2H_2O + 2e. \quad (6)$$

$$2C_2H_5OH + O_2^{-} = 2CH_3CHO + 2H_2O + 1e. \quad (7)$$

Thus, the electrons released from the surface reaction transfer back into the conduction band which increase the conductivity and lower resistance of SnO_2 as shown in Figure 6. The effect of chemisorptions has been discussed in details by V. S. Vaishnav et al. [7]. The gas sensitivity of the deposited SnO_2 thin film for ethanol gas also has been studied at concentration 100 ppm. The plot shown in Figure.7 represents the variation in the sensitivity with temperature and maximum sensitivity at a temperature of 305^o C.

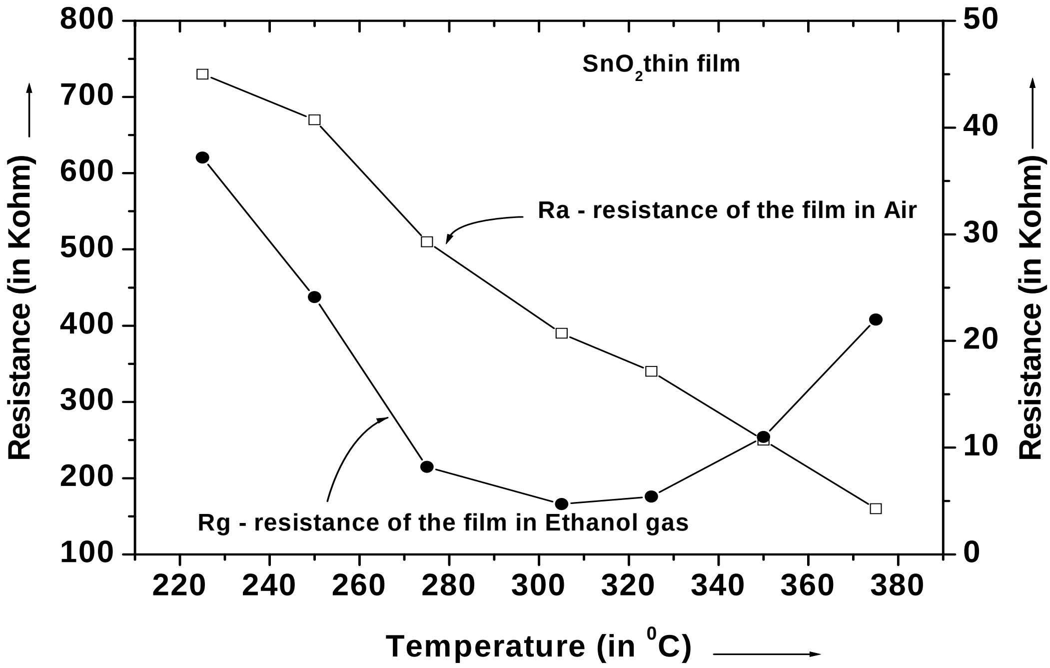

Fig. 6. Change in resistance in Air and Ethanol atmosphere at 100 ppm

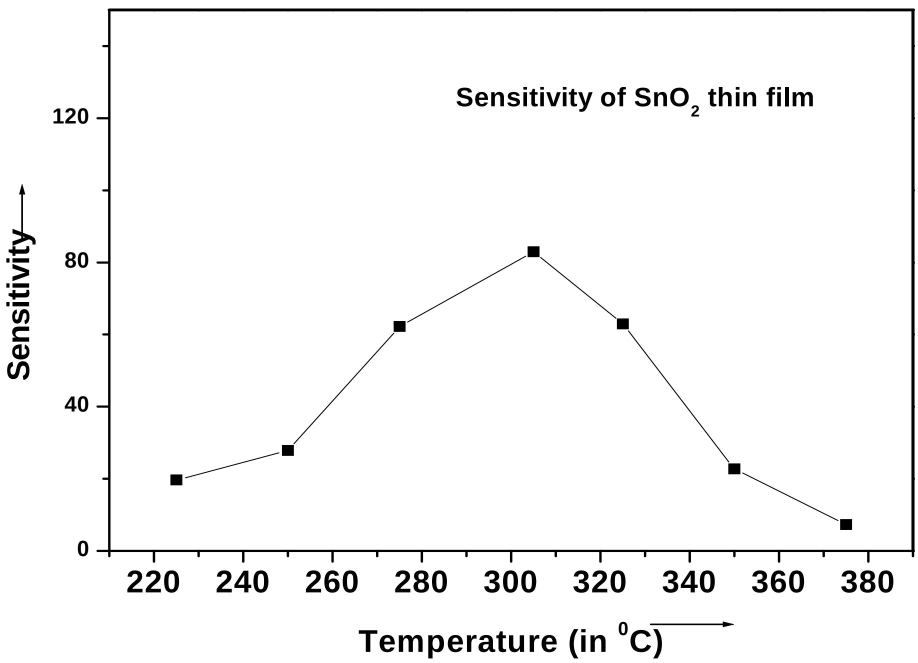

Fig. 7. Variation of ethanol gas sensitivity with temperature

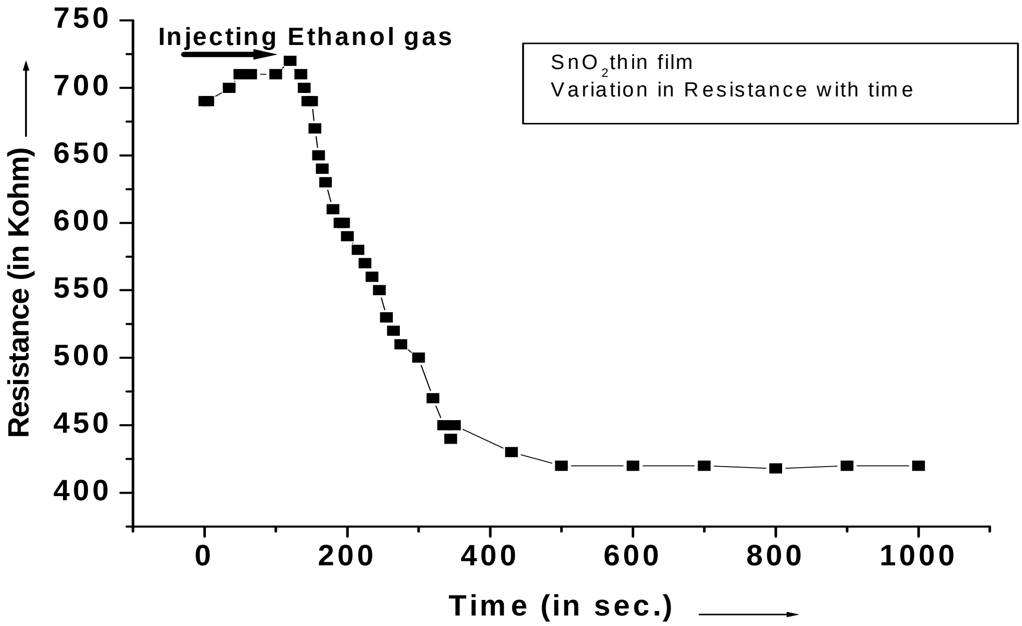

Fig. 8. Change in resistance of SnO_2 thin film in ethanol (100 ppm) with time

The variation of resistance with time show in Figure. 8. The rapid decrease in resistance has been observed in the time 170 sec. to 370 sec after injection of ethanol gas in chamber at 100 ppm gas concentration. This result reveals that within 200 sec the resistance of the SnO_2 thin film decreases 240 Kohm froms its normal value.

4. Conclusions

Transparent and conducting tin oxide film has been deposited by spray pyrolysis techniques. Structural, optical and gas sensing properties of the film studied as a function of temperature. The average grain size of the film is 48.6 nm at 300 ^{o}c and 51.02 nm annealed 400 ^{o}C . The observed direct band gap Eg is 3.71 eV and average transmittance is 78 %. The ethanol gas sensitivity of SnO_2 film is max. at 305 ^{o}C .

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