

Synthesis of SnO₂ Thin Film by Sol-gel Spin Coating technique for Optical and Ethanol Gas Sensing Application

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ABSTRACT

In this paper, Tin oxide (SnO_2) thin film synthesized by a simple spin coating sol-gel technique using non-alkoxide $SnCl_4.2H_2O$ as a precursors. The structural, optical, electrical and gas sensing properties of the film were studied by using XRD, SEM, TEM, FTIR, PL and UV–vis techniques. The X-ray Diffraction (XRD), shows the samples have a tetragonal rutile structure. The Transmission Electron Microscopy (TEM) shows the average particle size is of ~11.26 nm. Gas sensing performance of synthesized SnO_2 thin film was tested for ethanol gas at different operating temperatures as well as concentrations.

Keywords: Sol gel, SnO₂ thin film, Optical, Ethanol Gas sensing

I. INTRODUCTION

In recent years, Tin oxides a sort of n-type semiconductor material have attracted a lot of interest due to their fascinating features, i.e high surface-tovolume ratio [1], strong carrier confinement [2], enhanced surface modes in their Raman spectra [3], and high transmittance and electrical conductivity [4]. These properties leads to applications in catalysis, gas sensing, and optoelectronics such as light emitting diode, Solar cells and panel displays [5-7] etc. The applied synthesis procedures have seen to affect substantially the crystallinity, microstructure and defect structure of the nanorodes. Several methods including sol-gel [8-9], hydrothermal [10], electrospinning [11] have been utilized to synthesize SnO₂. Among these techniques, the sol gel method seems suitable due to its simplicity, easy to add doping materials, promising for mass production and low cost. The properties of SnO₂ were found to be dependent on the processing conditions and nature of precursors used. The precursors play an important role in growth, the structure and the morphology as well as optical and electrical characteristics of the doped material. For optical devices like Solar cells, panel displays applications mainly affected by signal loss and delay, we have to improve the conductivity without affecting the transmission.

Similarly, Tin oxide play an important role for applications in Solar photo-thermal conversion [12, 13]. Due to the limitation of solubility, these ions acts as grain growth inhibitors and remain aggregates at the grain boundaries. In the present work, sol gel synthesized spin coating method employed to obtain SnO_2 thin film at 500°C. The properties of Tin oxide on Crystallographic, Morphological, Optical and Gas sensing characteristics were studied. The obtained results are compared and discussed with several researchers.

II. METHODS AND MATERIAL

A. Synthesis

Nanocrystalline SnO_2 samples were prepared by a Sol gel rout using Sn precursors taken in the form of chlorides. In a typical synthesis process of SnO_2 , dissolve 5g of $SnCl_4$. $2H_2O$ from merck, India in 100 ml ethanol solution (Ethanol+ Water 1:1) and Stirred about 20 min until a transparent sol is produced. Add aqueous Ammonia solution (25% merck, India) drop wise to the solution under constant stirring and PH of solution was adjusted to a value up to 8. After 24 Hr of aging in the air resulting opal gel were centrifuged and washed with

Ethanol at least 5 times to remove ammonia, chloride impurity. The collected gel was dried in furnace over 80° C/4h in the air to remove moisture. Then after crush the sample and sintered at 500° C/4 Hr. Finally ashed coloured nanoparticle powders were formed [8, 14-15]. Fabrication of thin film for sensor based on the material is done by spin coating method on 10mm x 10 mm glass substrate at 4000 rpm, 30 sec and dry at 100° C for 1h, and then it was preheated at 350° C for 2 h and sintered at 500° C for 2 h in air.

B. Characterization techniques

First, the synthesized SnO₂ thin film were Characterized by X-ray diffraction (XRD) measurements using a Bruker D8 Advance diffractometer with monochromatic CuK_x radiation (λ =1.5406 A⁰) by recording θ in the range of $20-70^{\circ}$ in a step of 0.02° . To study the surface morphology & grain sizes, Scanning Electron microscopy(SEM) JEOL JSM 5600 with Resolution : 3.5 nm, Magnification : x18 to 300,000, Accelerating Voltage : 0.5 to 30 kV and Transmission electron microscopy (TEM) model JEOL/JEM 2100 was employed with acceleration voltage 200kV And 2000X - 1500000X magnification. ImageJ computer program were used to investigate the particle size distributions. Fourier Transform infrared (FT-IR) spectra of the powders were recorded using a Bruker, Germany, Model vertex 70 using the KBr pellet technique in the range 400 to 4000 cm⁻¹ with a resolution of 0.5 cm⁻¹. Photoluminescence (PL) studies of prepared samples were carried out using a F-4500 FL spectrometer with 150 W Xenon lamp at room temperature. UV-Vis measurement was recorded using Jasco Spectrophotometer V-770 in a 200-1000 wavelength domain.

Finally, ethanol gas sensing measurement is carried out using gas sensing chamber, the change in resistance of sensors were recorded by NI USB 6210 DAQ on PC.

The sensor sensitivity is defined as S = Ra/Rg, Where, Ra is the resistance in ambient air and Rg is the resistance in tested gas. Similarly, ethanol gas response time and recovery time were also recorded.

III. RESULTS AND DISCUSSION

A. XRD

To study the crystallite size, crystal structure and lattice parameters of SnO_2 , XRD analysis was used. The X-ray diffraction patterns of SnO_2 nanoparticles sintered at 500^{0} C shown in Fig.1.



b) Texture Coefficient of SnO₂

The peaks were indexed using Powder X software and they are matched with the tetragonal rutile structure of SnO_2 , which are consistent with the values in the standard card (JCPDS 77-0452) with a maximum intensity corresponding to (110) plane [16]. Further it has been observed that lattice parameters a and c are calculated using unit cell software program and cell volume as shown in (Table 1). All calculated values are in good agreement with the reported values (JCPDS 77-0452).

Moreover, the texture coefficient (TC) gives information the maximum preferred orientation along with the diffraction plane, means the increase in the preferred orientation is related with the increase of the number of grains along that plane. $TC_{(hkl)}$ values are calculated from XRD data[17]:

$$TC_{(hkl)} = \frac{I(hkl)/I_0(hkl)}{N^{-1}\Sigma I(hkl)/I_0(hkl)} - \dots - (1)$$

Where, I(hkl) is the measured intensity of X-ray data, $I_0(hkl)$ is the corresponding intensity taking from the JCPDS 77-0452 card and N is the number of diffraction peaks observed in the XRD pattern. TC is one of the parameter important structural to secure the implementation of the prepared materials. Agashe et al. [18] reported that (200) preferred orientation of SnO_2 thin films, are suitable for many optoelectronic and gas sensing application. Che et al. [19] reported that SnO_2 surface having a very high reactivity for the oxidation reactions due several chemisorbed oxygen species exist. It is clear from the sample that if TC>1, this implies that crystal growth occurs in certain preferred orientation. And TC=1, represents randomly oriented crystallites presents. Figure 1.b) graphically represents preferred orientation of the crystallite.

On the other hand, the average size of the crystalline grains of the sample was calculated using at full width half-maximum(FWHM) and Debye-Scherer's formula[20] given by :

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} - (2)$$

Here, D_{hkl} is the crystalline size, λ is the X-ray wave length, β is the (110) full width at half maximum (FWHM) and θ is the angle of diffraction. The estimated sizes at the most intense crystallographic plane (110) are given in Table 1. The crystallite size of the pure SnO₂ nanoparticles are laying between 12nm. The ratio of the lattice parameters a and c is a measure of lattice distortion, it has been calculated from XRD data (Table 1). From the above discussion, it can be concluded that the narrowing or broadening of the XRD peaks of SnO₂ occurred due to atomic diffusion and lattice strains and not by lattice distortions. The particle size calculated by Scherer formula for SnO₂ have been further validated by Transmission Electron Microscopy (TEM) observations. Increase in Unit cell volume shows expansive strain in the particles and decrease in unit cell volume shows compressive strain in the particles.

On the other hand, geometric mismatch between crystalline lattices of thin films and substrate may develop stresses [21], and these stresses can cause microstrains (ζ) in the films. The microstrain values are calculated by following relation [22]:

 $\zeta = (1/\sin\theta) \left[(\lambda/D) - (\beta \cos\theta) \right] -----(3)$

Where, β is FWHM of (110) peak and D is the average grain size.

Dislocation is one of the important factor to investigate growth mechanism. It plays a important role in the variation of electrical resistance because the increase in the dislocation density gives rise in disorders, crystal defects in lattice and decreasing crystallinity. Dislocation density (δ) gives information on length of dislocation lines per unit volume (lines/m²). It can be estimated by following relations [22].

$$\delta = 1/D^2$$
 -----(4)

The all calculated values of ζ and δ are given in table 1.

Table 1: The calculated values of the grain size, lattice parameter, microstrain dislocation density(δ), Intensity.

	D _{XRD} (nm)	a (Å)	c (Å)	c/a	a ² c (Å ³)	strain ξ (X10-4)	δ (x10 ¹⁴ line/m ²)	Intensity 110
SnO ₂	12	4.740	3.184	71.555	71.53	19.45	59.17	717





Figure 2: a) SEM and b), c), d) TEM images of SnO_2 at $500^{0}C$

Fig.2 a) shows the typical morphology of SnO_2 nanoparticles. Powder samples were used for SEM analysis. Powder was stick on the sample holder using double sided tape and gold coated with sputter coater. It is seen that SEM image of SnO_2 microstructure of these powder samples shows the presence of large spherical aggregates of smaller individual nanoparticles with variations in particles size.

Due to the large surface and high surface energy of primary nanoparticles, Tin Oxide tiny particles are prone to aggregated [23]. The randomly grown grains gives rise in scattering effect, which reduces the transmittance [24]. The surface state of such oxide nanoparticles influence there optical and electrical properties which are essential to ensure the implementation of the different optoelectronic devices and gas sensors.

Fig.2.b) Shows TEM image of prepared SnO_2 nanoparticles showing an average diameter of about 11.26 nm as well. For this powder samples were dispersed in ethanol and sonicated in an ultrasonic bath. The particle size obtained from TEM analysis is slightly higher than the crystalline size calculated from XRD data.





FT-IR spectra were recorded in solid phase by using KBr pellets technique in the region of 400-4500cm⁻¹. FT-IR spectra of pure SnO₂ nanoparticles prepared at 500^oC are shown in figure 3. The observed frequency at 450 cm⁻¹ is assigned to the symmetric Sn-O-Sn stretching mode. Antisymmetric Sn-O-Sn stretching mode of the surface hydroxyl groups is obtained at 650 cm⁻¹ is observed. The broad band between 500 to 800cm⁻¹ due to the vibrations of Sn-O-Sn mode of tin oxide [8,25-26]. The peak at 1000 cm⁻¹ is related to the vibrations from 1300-1600 cm⁻¹ is assigned to the C-O stretching mode [27-28]. The bands appearing in all the samples around 1650 cm⁻¹ might be due to the bending mode of O-H bonds. Lastly, the broad band appearing in the

region 2500-3500 cm⁻¹ may be due to vibration of adsorbed water. The present assignments corroborate well with the values very near to the reported available literature [29-31].

D. Uv-vis

Fig.4 a) shows the absorption coefficient $\alpha(\lambda)$ of SnO₂ thin film from 200 to 1000 nm range. Samples showing low absorption at higher wavelength and strongest absorption at lower wavelength. The absorption spectra between 200 to 450 nm, shows a maximum around 200 and 300 nm, which indicates the photo-excitation of electrons from the valence band to the conduction band. It is well established that the absorption depends on several factors such as crystalline size, surface roughness, defect density etc. Hence, only the structural study did not reveal significant changes in the morphology of the samples. For that we have to increase of the absorption to increase of the density of the defects and disorder, which are very related to the to the reduction of crystallite size. Indeed, an increase in dislocation density values and microstrain gives rise to crystal defects and disorders in Tin oxide lattice [24]. Thus, with more defects, the electronic transitions from the filled valence band to the energy level of defects.

On the other hand, In order to calculate the optical band gap (Eg) we used the Tauc's relation,







Figure 4: a) Absorption and Transmittance b) Tauch Plot c) Urbach Energy pattern of SnO₂ thin film.

Where, α is the absorption coefficient, A is a constant while the exponent n depends on the type of transition (n=2 for indirect allowed, n=1/2 for direct band gap semiconductor). Therefore, the optical band gap is obtained by extrapolation of the linear region of a tauc's plot by plotting $(\alpha hv)^2$ vs hv . The Tauc's plot of SnO₂ samples are shown in Fig.4 b). The measured band gap Eg was found to be 3.15 eV, which is slightly less to the reported values of bulk SnO₂ i.e 3.6 eV [32]. It can be seen that the band gap values shows decrease tendency in Tin oxide structures. This can be attributed due to quantum confinement effect [33], reorientation effect [34], microstrain and dislocation density in nanoparticles. Thus, many researchers reported that, with higher level of defects, the electronic transitions occurs from the filled valence band to the energy levels of defects instead of the filled valence band to empty conduction band. These phenomena leads to band tail and shrinkage of the band gag i.e Burstein Moss shift [35]. Fig.4 a), shows the optical Transmittance spectra of SnO₂ thin film in the wavelength region 200 - 1000 nm. These spectra show that the prepared film exhibit a transparency coefficient lying between 65 to 95 % in the visible range. The Urbach E_U or band tail energy which characterizes the width of the located state and is associated with microstructural lattice disorder. The Urbach E_U values were obtained from the inverse of the slop of $Ln(\alpha)$ vs (hv) Fig. 4 c) of SnO₂ thin film and calculated value is found to be 0.5 eV.

E. PL

PL study can give us significant information on the energy states of impurities and defects, which are useful in study the structural defects in Semiconductors. The room temperature PL behavior of SnO_2 thin film was investigated using PL spectrometer. Fig.5 a) contains the photo induced fluorescence spectra for an excitation wavelength 400 nm. It can be seen from the PL spectra the film exhibit broad emission at 200 to 250 nm and one emission peak at 220 nm.

This emission bands presents due to essentially to the presence of point defects, such as oxygen vacancies in SnO_2 film [36-37].

Fig. 5 b) shows room temperature PL excitation spectra (at $\lambda em = 300$ nm) for SnO₂ film. The 2 broad excitation bands are observed at 350-450nm and 450-500 nm at constant emission 300nm. The major peaks are observed of SnO₂ at 350 to 450nm band with very poor intensity, but at 450-500nm the highest peaks observed are 405nm and 470nm.



Figure 5 a): PL Emission Spectra of SnO₂b): PL Excitation spectra of SnO₂

F. DC Electrical Conductivity



Figure 6: Conductivity of SnO₂ thin film

The DC electrical conductivity of SnO₂ thin film was measured using two probe method in the 30–400 °C temperature range, Fig. 6 shows the curve of DC electrical conductivity as a function of temperature. It can be measured that the conductivity of the film increases with temperature, the room temperature dc electrical conductivity is found to be in the range of 6.05 $\times 10^{-8}$ S/cm and after heating is increased to 5.49 $\times 10^{-6}$ S/cm at 300 °C. This shows the thermally activated conductivity behavior of SnO₂ thin film [38]. Which indicates the conductivity increases with the temperature.

Inset of Fig. 6 shows the plot of Ln σ versus 1000/T, From the slope of the Ln σ versus 1000/T curve, activation energy was calculated using the relation [38]:

$$\sigma = \sigma_0 \exp(-Ea/kT) - \dots - (6)$$

where, Ea is the activation energy, k is the Boltzmann constant , T is the temperature, and σ_o is the constant of proportionality. The activation energy of an electrical conduction is found to be 0.61 eV. This activation energy value indicates that the activation of electrons is excited from donor levels to the conduction band, as the temperature is increased. With increasing temperature, more charge carriers overcome the activation energy barrier and these carriers participate in the electrical conduction [38].

G. Gas sensing performance

Effect Temperature and concentration on gas response:

The Gas sensitivity of tin oxide as a function of operating temperature range 150 to 350° C and Ethanol gas concentration (100 -1500 ppm) is displayed in Fig. 7. Fig. 7 shows sensitivity variation of tin oxide sensor at 150-350°C towards 100-1500 ppm of ethanol gas. It is observed that highest sensitivity is achieved under exposure to 1500 ppm of ethanol gas at 250°C for tin Oxide thin film sensor.



Figure 7: Ethanol gas sensitivity Pure SnO₂

From Fig. 7, it concludes that sensitivity increases with an increase in the operating temperature, reaching maximum value corresponding to 250° C. However, further increasing the temperature above 250° C ethanol sensitivity start to decrease again. The optimum sensitivity can be attributed due to thermal energy obtained was high enough to overcome the activation energy barrier of the reaction, while reducing gas sensitivity was due to the difficulty in exothermic gas adsorption [39].

The gas sensing mechanism :

The SnO_2 thin film based gas sensing mechanism is mainly based on a change in the electrical resistance due to the oxygen adsorption and reactions of the gases adsorbed on the sensor surface. Also, operating temperature affects the properties of the materials and leading to a difference in the gas sensitivity. It has been observed that, metal oxides mostly sense gases at higher operating temperatures. The operating temperature creates oxygen species on the sensor surface which play an important role in the gas sensing phenomena. The absorption of oxygen depends mainly on the type of materials and their oxidation/reduction reaction with the gas. The following reactions shows how oxygen adsorbed on the sensor surface [40]:

$$O_{2 (gas)} \leftrightarrow O_{2 (ads)} \qquad -----(7)$$

$$O_{2 (ads)} + e^{-} \leftrightarrow O_{2^{-} (ads)} -----(8)$$

$$O_{2 (ads)} + e^{-} \leftrightarrow 2O^{-} (ads) -----(9)$$

$$O^{-}_{(ads)} + e^{-} \leftrightarrow O_{2 (ads)} \qquad -----(10)$$

Where, O- is the oxygen adsorption, e- are electrons. In metal oxide semiconductors, oxygen ions (O-) work as an acceptor at the surface of the film. When the reactive gas is adsorbed on the surface of a sensor, this may lead to changes in the resistance value of the thin layer of the gas sensor. The ethanol sensing mechanism of SnO₂ thin film could be explained as, ethanol is a reducing gas, when the samples exposed to ethanol at the higher temperature, they remove the adsorbed oxygen, restore electrons to the conduction band and decrease the resistance of the semiconductor.

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The response time is, the time taken by the sensor element to achieve 90% of stable output when the gas was introduced. The recovery time is, the time taken by the sensor element to reach 90% of its original value. Fig. 8 shows the response and recovery time of SnO_2 sensor at 250°C and 100-1500 ppm ethanol gas. It is observed that when the target gas was inserted in the gas sensing chamber the resistance of the sensor decrease drastically. However, when air was introduced resistance regains its original value. The time measured between response and recovery is shown details in Fig. 8.



Figure 8: Variation of Response and Recovery Time of SnO₂ sensor of ethanol concentration.

Reproducibility and stability study of SnO₂ sensor:



Figure 9 Reproducibility of SnO2 sensor to 1500 ppm of Ethanol gas



Figure 10: Stability study of SnO2 Sensor

To study the reproducibility of SnO₂ thin film sensor, the SnO₂ gas sensing test was repeated three times at 1500 ppm gas concentration and at 250 °C operating temperature, shown in Fig. 9. It is revealed that the gas response of the SnO₂ sensor towards ethanol is nearly constant confirming the reproducibility of the sensor. In order to investigate the stability of the SnO₂ sensor at 1500 ppm concentration of ethanol gas and at operating temperature of 250 °C, the gas response of the film was measured for 60 days at an interval of 15 days and the result is shown in Fig. 10. From the figure, it is seen that the gas response dropped initially and after 30 days nearly constant with 57% stability. This decrease in the gas sensing response with the number of days can be attributed to the formation of layer oxides/moisture [39]. Thus, it can be concluded that the sensor with high response/selectivity and low response/recovery times based on SnO₂ thin film can stand as good sensor for detection of ethanol gas.

IV. CONCLUSION AND OUTLOOK

This paper deals with some structural, optical and Ethanol gas sensing characterization of obtained spin coated thin film by sol gel method at 500^oC. The XRD study shows that the obtained powder have rutile tetragonal structure. SEM images reveal the presence of agglomerates. TEM image confirms that its size closely matches with XRD value. Second, PL emission and excitation peaks investigated for photocatalytic applications. UV-vis has successfully investigated to obtain band gap and band tail value of film. Finally, Ethanol gas Sensitivity, Response time, Recovery time, reproducibility, stability was studied by SnO₂ spin coated thin film sensors. The experimental result indicates that SnO₂ sensor exhibited highest sensitivity at 250°C temperature.

V. ACKNOWLEDGEMENT

The auther gratefully acknowledge the UGC-DAE Center, Indore for XRD, SEM, FTIR and SAIF, kochi for TEM. We need to convey our thanks to Dr. R. S. Ningthoujam, Chemistry Division, BARC, Mumbai for PL measurement.

VI. REFERENCES

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