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Tin Oxide Thin Film Synthesized by Sol-Gel and Thermal Evaporation Techniques for Gas Sensors

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Abstract*: In this study, pure semiconductor tin oxide (SnO_2) thin films have been deposited on glass substrate by Thermal Evaporation and Sol-Gel techniques for gas sensing applications. Structural, micro structural, optical and gas sensing properties were studied and compared. In both the cases thickness of the films were maintained in between 490-500nm. The films were annealed at 500^0C for one and half hours. The structural study of the films was carried out by XRD measurement using SIEMENS diffractometer (Model) D 5000. The tetragonal rutile structure of SnO_2 was confirmed by the present investigation. Surface morphology was examined from SEM micrographs by using Scanning Electron Microscope Model – Philips XL 30. From this study the grain size was found to be around 40-45 nm. Optical characteristics were studied by UV/VIS Spectrophotometer Model ELICO-SL-159 in the wavelength range 300-1100nm. From this data optical properties like refractive index, thickness of the thin film and band gap were calculated. The measured refractive index was 2.14 which is nearly the same with the result obtained by Manifacier et al. The films were investigated for sensing of carbon monoxide gas. Sensitivity test was carried out by a hand make sensitivity tester. Sensitivity of the film to CO gas was measured at different temperatures and was found to be highly sensitive at 220^0C for the film prepared by thermal evaporation and 235^0C for the film prepared by Sol-Gel technique technic at 50 ppm.*

Keywords: SEM, Sol-Gel, Thermal Evaporation, Tin Oxide, XRD

1. Introduction

Since last two decades researchers have been engaged to solve the environmental pollution problem which is a great concern throughout the world due to exhaust of combustible and process gases mostly from industry and motor vehicles. It is a great challenge in front of researchers. Due to development of solid state semiconducting gas sensors it became little easy to control and safely monitoring the pollutant gases over the other technologies like gas chromatography, FTIR spectroscopy etc. Generally semiconducting transparent materials have vital role in sensing technology due to the properties like high transmittance, high band gap, sustainable at high temperature and mechanically hardness. Semiconducting sensors are reliable, easy to miniaturize, less cost, easy to produce and can be designed to operate over a wide range of conditions. Recent days, it is relatively easy to synthesized semiconducting gas sensors due to development of thin film technology. Tin Oxide thin film is more transparent in the region of visible spectrum. It has high band gap and having high electrical conductivity due to free electrons in oxygen vacancy holes. Due to above properties, tin oxide thin films are used extensively in transistors [1], transparent conductive electrode for solar cells [5], Protective and wear-resistant coating on glass containers [11] and for gas-sensing and gas monitoring devices [8],[3], liquid crystal display [2]etc.

In this paper we describe the preparation and study of optical properties and sensing characteristics of Tin Oxide (SnO_2) synthesized by Sol-Gel Dip coating and Thermal evaporation techniques. In dip coating method we started with Tin(II) Chloride which was preferred due to low cost as precursor, methanol as solvent and glacial acetic acid as chelating agent and we prepared a transparent solution. SnO_2 thin film was synthesized on a glass substrate by sol-gel dip coating technique. Similarly, tin oxide thin film was synthesized by thermal evaporation technique from tin oxide (SnO) powder 99% pure from Aldrich and then both the films were studied for the optical, morphological and carbon monoxide gas sensing.

2. Preparation of Film Sol-Gel

The glass substrates were thoroughly cleaned with cleaning liquid soap and then with acetone and finally with ultrasonic cleaner. 1gm of anhydrous tin(II) chloride ($SnCl_2$) was taken in a beaker and 50ml of methanol(CH_3OH) with 1gm glacial acetic acid(CH_3COOH) was added to it and stirred by a magnetic stirrer for 45 minutes at NTP to get a clear and homogeneous solution. Then the cleaned substrates were

dipped in the prepared solution by means of Dip Coating Unit model no.-HO-TH-01 as shown in the figure 1. The coated substrates were dried at 150^0C in a muffler furnace for 1hr and then heat treated at 300^0C for about 15 minutes. The above procedure was repeated for four times to get the desired thickness of around 500nm. After getting the required thickness finally heat treatment was carried out on each substrate at 500^0C for one and half hour in a furnace (INDFURR).

Figure 1: Dip Coating Unit

2.2 Thermal Evaporation

Tin oxide thin film was also synthesized by thermal evaporation technique from pure tin oxide (SnO) powder. Tin oxide powder was taken in a boat and connected to the electrodes as shown in the figure 2. The pressure of the chamber was maintained at 2.5 x 10^{-5}torr and rate of deposition fixed at 6-8 A^0/sec at substrate temperature 40^0C. During the process the target and source was maintained at 10 cm apart.

Figure 2: Thermal Evaporation Unit

3. Results and Analysis

3.1 Optical

The optical properties were carried out by the equipment ELICO UV/VIS spectrophotometer (Model – SL- 159) in the wavelength range 300nm to 1100nm.The refractive index and the thickness of the film were calculated using the formula [10],[12].

$$n=\left\{\left(2\mu\frac{T_u-T_l}{T_uT_l}+\frac{\mu^2+1}{2}\right)+\left(\left(2\mu\frac{T_u-T_l}{T_uT_l}+\frac{\mu^2+1}{2}\right)^2-\mu^2\right)^{1/2}\right\}^{1/2}$$

$$\text{and } d=\left|\frac{\lambda_1\lambda_2}{4(n_1\lambda_2-n_2\lambda_1)}\right|$$

Where 'n' and 'd' are the refractive index and thickness of the thin film, 'μ' refractive index of the substrate, T_u and T_l be the transmission maximum at upper envelop and transmission minimum at lower envelop for a particular wavelength λ, n_1 and n_2 be the refractive index of the thin film at maxima(for wave length λ_1) and corresponding minima (for wave length λ_2) where phase difference is π.

The transmission % Vs. wavelength curve was plotted from the data obtained from transmission spectrum and is shown in the figure 3.

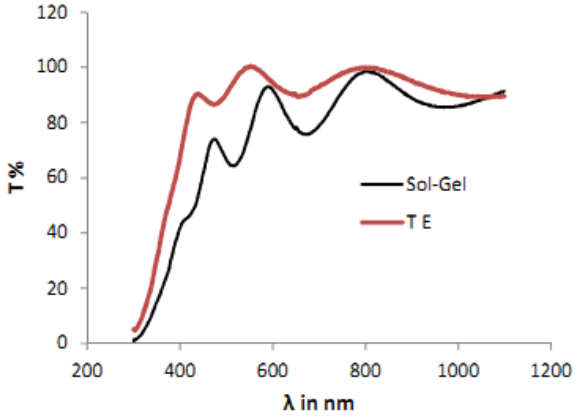

Figure 3: Transmission Vs. Wavelength

From figure 3 it was clear that transmittance is more in case of film prepared by thermal evaporation method than Sol-Gel Method. It may be due to high porosity and larger grain size and less absorption in the film deposited by thermal evaporation method. It was also clear that transmission values were more than 0.80 at wave length greater than 500nm in both the cases. From the Transmission Vs. wavelength graph average refractive index was calculated as 2.14 and 2.18 for films prepared by Sol-Gel and Thermal Evaporation respectively. The thickness was maintained at 500nm. The band gap [11] was calculated from the graph $(\alpha h\nu)^{1/2}$ Vs. hν as shown in figure 4.

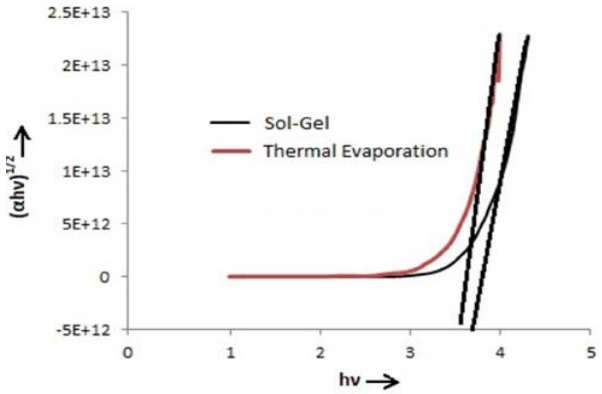

Figure 4: (αhν)½ Vs. hν for SnO2 film

It has been observed the band gap was 3.65eV and 3.52eV in case SnO_2 thin film deposited by Sol-Gel and Thermal Evaporation technique respectively. This band gap value suitably matches the values given by J.E. Dominquez [4] . The less band gap of the film deposited by thermal evaporation technique may be due to improvement of the degree of crystallization and growth of grain.

3.2 Structural

XRD measurement was carried out by Siemens Diffractometer Model- D 5000 using CuKα having wavelength λ= 1.540^{0}A radiation with a diffraction angle 20^0 to 65^0. The graphs are shown in fig 5 and 6.

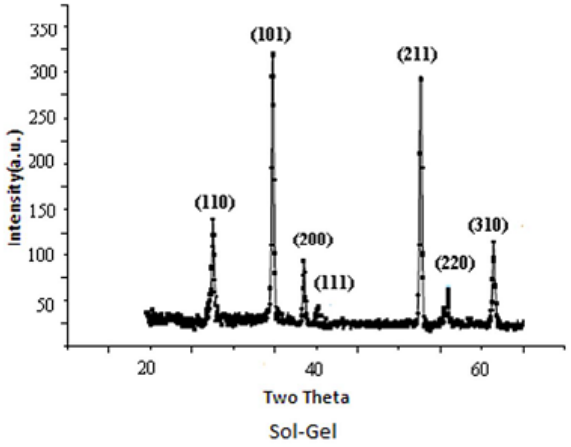

Figure 5: XRD- Sol-Gel

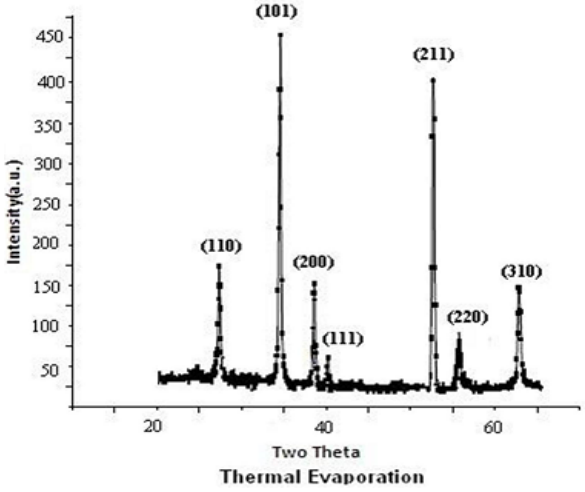

Figure 6: XRD-Thermal Evaporation

From the graph it was clear that in both the cases well defined sharp diffraction peaks were seen nearly at same angle of 2θ which may be considered to be the crystalline tetragonal rutile structure of SnO_2(JCPDS Card No. 88-0287).XRD peaks were very narrow and sharp which shows higher crystalline quality of the SnO_2 film. The (101) peak has the largest intensity in both the cases, so it may be believed the preferential growth along direction (101) hence Sn forms an interstial bond with oxygen and exist as rutile SnO_2.

The figure depicts a significant increase in the intensity of the X-ray diffraction peaks in case of thermal evaporation this may be due to additional nucleation centers for the SnO_2 growth due to which grain size also increased.Grain size of the particles was determined by using Debye-Scherrer formula $D = \frac{0.94\lambda}{\beta \cos\theta}$, the symbols are having their usual meaning . Using the above formula the average grain size of the deposited film was calculated as 45.24 and 40.18nm for the film grown by thermal evaporation and sol-gel technique respectively. This difference may be probably due to the presence of strains distributed unevenly in the film.

SEM measurement was carried out by Scanning Electron Microscope Model- Philips XL 30. SEM micrograph are shown in the figure 7 and 8 which shows agglomeration of the grain particles in both the cases.The grain size calculated is about 48nm and 44nm for thermal evaporation and Sol-Gel technique. From the SEM images it was clear that microstructural properties as well as grain size changes a little due to method of preparation. SEM micrograph of thin film contains domes like structure and the size of the domes were more or less same size in both the cases. This dome like structures may be believed as the top surfaces of the grains of the film.

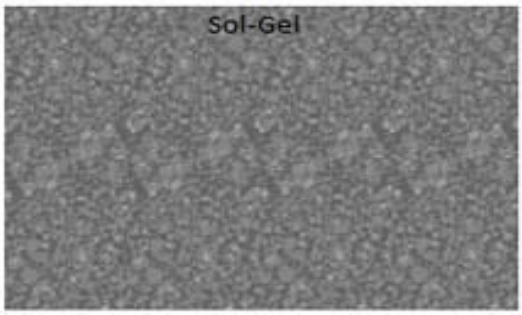

Figure 7: SEM-Sol-Gel

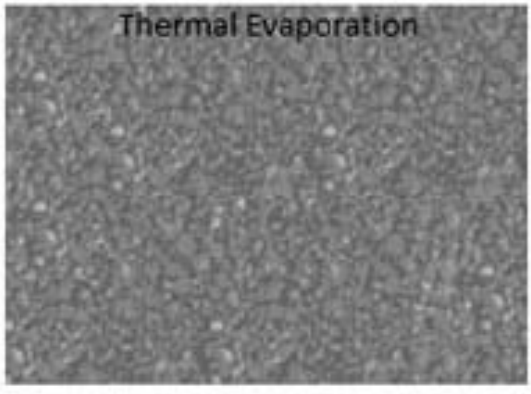

Figure 8: SEM-Sol-Thermal Evaporation

3.3 Gas Sensitivity Analysis

According to Stoichiometric, tin oxide is an insulator at room temperature. But when thin film of tin oxide comes in contact with air, the surface of the film absorb oxygen [6] at grain boundaries which ensnare electrons and build a barrier around each grain [7] which behaves like doping, and produces ionization levels close to the bottom of the conduction band and finally exhibits the property of n-type semiconductor with a band gap (≈3.6 eV)[9]. When thin film of SnO_2 was exposed to air, oxygen from the air is adsorbed onto the surface of the SnO_2 thin film. Electrons from the surface region of the SnO_2 are transferred to the adsorbed oxygen, leading to the formation of an electron-depleted region near the surface of the SnO_2 film. The electron depleted region, where electron density is less, is an area of high resistance and the core region of the film, where electron densities are high, is an area of relatively low resistance. Now the adsorbed oxygen becomes O^- and O_2^- species. When the thin film of SnO_2 is exposed to a reducing gas like CO, surface reactions such as $CO + O^-_{ads} \rightarrow CO_2 + e^-$ and $2CO + O^-_{2,ads} \rightarrow 2CO_2 + 2e^-$ took place. Due to which electrons releases and the electrons released from surface reaction transfer back into the conduction band leading to a decreasein the resistance or increase in conductance of the SnO_2 thin film.

The sensitivity of the SnO_2 thin film for carbon monoxide gas has been studied at concentration 50ppm. The variation of the sensitivity with temperature is shown in the figure 9.

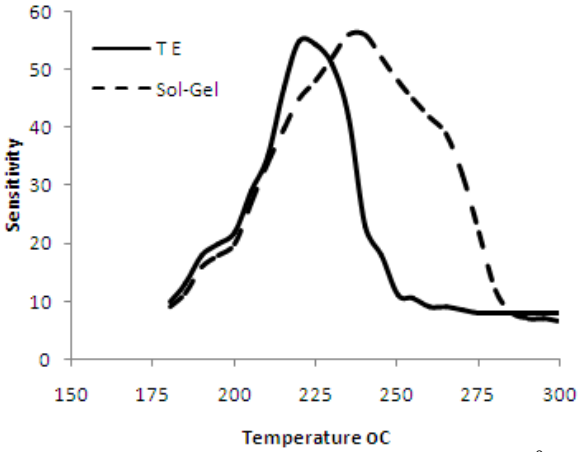

Figure 9: Sensitivity Vs. Temperature in ^{0}C.

Figure 9 depicts that maximum sensitivity occur at temperature of 220^{0}C for Thermal Evaporation Technique and 235^{0}C for Sol-Gel technique. At low temperatures there is less oxygen coverage, when the sensor is exposed to air and therefore when the target gases are introduced there is negligible change in sensitivity. As the operating temperature increases, number of adsorbed oxygen species would have reacted more and more number of electrons which are released due to this reaction sent back to conduction band i,e desorption rate of adsorbed gases also increases with increasing temperatures.

4. Conclusion

Tin oxide thin films were synthesized by Thermal evaporation and Sol-Gel technique. From optical measurement the band gap was measured as 3.65eV and 3.52eV in case SnO_2 thin film deposited by Sol-Gel and Thermal Evaporation technique respectively. XRD and SEM study revealed the grain size is more incase of the film synthesized by thermal evaporation method. The film was studied for carbon monoxide gas sensing. It was observed that the sensitivity of the film for CO gas at 50 ppm was more at 220^{0}C for thermal evaporation technique and 235^{0}C for sol-gel technique which may conclude that tin oxide film synthesized by thermal evaporation method is better for gas sensing than sol-gel method due to more surface area is available to expose.

5. Acknowledgement

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