Carbon Monoxide Sensitivity of Tin Oxide Thin Film Synthesized by Sol Gel Method

Sumanta Kumar Tripathy[1,*] and Bhabani Prasad Hota[2]
[1]*GVP College of Engineering (Autonomous), Madhurawada, Visakhapatanam, A.P., India*
[2]*Godavaris Mahavidyalaya, Banpur, Khurda, Odisha, India*

The present paper is about the synthesis of Tin Oxide (SnO_2) thin film on glass substrate by sol-gel dip coating method and annealed at 500^0C for one and half hour. The grain size which plays a vital role in gas sensing was measured from XRD data and found to be 48.54nm by using Debye Scherrer formula. Carbon monoxide gas sensing of the film was measured at different temperature and was found to be highly sensitive at 220^0C at concentration 50ppm. The prepared film was investigated for response time and was found that the sensor responded quickly to carbon monoxide gas at about 20 sec. The optical characteristics were studied by using ELCO UV/VIS spectrophotometer Model- SL 159 in the wavelength range 300nm to 1000nm. The result of change in conductivity of the sensor in presence of CO gas was reported.

1. Introduction

Environment pollution is monotonically increasing due to combustible and process gases mainly from industry and motor vehicles. To protect environment it is essential to control and safely monitor the pollution. Different methods like gas chromatography, infrared spectroscopy, semiconductor gas sensors and many others have been used to detect and monitor the pollutants. But solid state semiconducting gas sensors have considerable advantages than the other gas detection techniques. Semiconducting sensors are reliable, easy to miniaturize, less costly, easy to produce, and can be designed to operate over a wide range of conditions. It can also operate at high temperatures. Semiconducting sensors can be designed for sensing of multiple species simultaneously and also detection limits are in the range of part per million levels (ppm).

It is a fact that the sensor characteristics can be changed by varying the crystal structure, dopants, preparation method, operation temperature, etc. Nonetheless, highly specific metal-oxide sensors are still not available. In recent years, the interest of researchers and engineers to gas sensitive materials has grown substantially due to the progress in thin film technology. Many semiconducting metal oxides have been used as gas sensors. But Tin Oxide (SnO_2) is the most important material used in gas sensing applications in domestic, commercial and industrial sectors. Tin Oxide gas sensors are presently the right choice of researchers due to their high electron mobility, low operating temperature, high sensitivities, high chemical stability, mechanical simplicity of sensor design, and low manufacturing cost.

Development of gas sensors using un-doped/ doped SnO_2 for the detection of gases like NO_2 [1], CO [2-4] H_2 [5-6] NH_3 [7], H_2S [8-9] has already been reported. But the gas sensor for the detection of carbon monoxide gas which is contained in automobile exhaust along with nitrogen oxides is the most important environmental contaminant and represents a challenging job for researchers. Lim et al., Qian et al., and Ramirez et al. have studied the detection of CO gas at a temperature of 400^0C, 250^0C-300^0C and 295^0C, respectively, with sensing materials ZnO, SnO_2Au and SnO_2, respectively. But the present paper describes the detection of CO gas at low temperature of 220^0C by synthesizing thin film of SnO_2 on glass substrate by sol-gel method. Till today so many methods were adopted to synthesize doped or un-doped tin oxide films such as Thermal Evaporation [10-11], Chemical Vapor Deposition [12-13], R.F. Magnetron Co-sputtering [14] Laser Pulse Evaporation [15-16], Spray Pyrolysis [17-18], ultrasonic spray pyrolysis [19], and sol-gel [20-22]. Among these techniques, the Sol-gel method plays an important role due to several advantages such as simple experimental arrangement, easy control on film thickness with a high porosity area, which can improve the efficiency of the sensors, less processing cost, greater homogeneity and more purity.

In this study, we adopted dip coating method. Starting from Tin(II) Chloride, which was preferred due to low cost as precursor, methanol as solvent and glacial acetic acid as chelating agent, a transparent solution was prepared and SnO_2 thin

---

[*] sktripathy2009@gmail.com

film was synthesized on a glass substrate by sol-gel dip coating technique. The optical properties were studied from the interference fringes of the transmission spectrum, which was carried out by the equipment ELCO UV/VIS spectrophotometer (Model – SL-159) in the wavelength range 300nm to 1000nm. Structural analysis of the films was carried out by XRD measurement using SIEMENS Diffractometer (Model D5000). The study confirms rutile tetragonal structure of SnO_2.

2. Experimental Details

2.1. Synthesis of thin film

In a conical flask, 1gm of anhydrous tin (II) chloride ($SnCl_2$) was dissolved in 50ml of methanol (CH_3OH) with 1gm glacial acetic acid (CH_3COOH) and continuously stirred by a magnetic stirrer for 45 minutes at NTP to get a clear homogeneous solution. Then the glass substrate on which thin film will be deposited was thoroughly cleaned with cleaning liquid soap and then with acetone to remove organic particles on the surface and then washed with distilled water. It was then soaked in TEA diluted isopropyle alcohol for 10 minutes and then dried.

Now the substrate was dipped in the above prepared solution by hand and moved out with the same speed. The coated glass substrate was dried at 150^0C in a muffler furnace and then heat treated at 300^0C for about 15 minutes. The above procedure was repeated for a number of times to get the desired thickness. In this paper, we had repeated the procedure for six times to get a thickness of 645nm. In this dipping process there will be two sided coat on the substrate. For optical transmission measurements the film on one side of the substrate is required, so other side coat was removed by means of a sharp edge. While removing the coat precautions were taken so that the other side coat would not be disturbed at all. Then finally heat treatment was carried out on substrate at 500^0C for one and half hour in a muffler furnace in air.

2.2. Mechanism of sensing

The change of electrical properties of the metal-oxide semiconductor due to adsorption of gas molecules is responsible for SnO_2 sensor response, which is due to surface interactions between the tin oxide and the surrounding gases. The steps involved in sensor response upon exposure to air and to a reducing gas, are described below. When thin film of SnO_2 was exposed to air, oxygen from the air was adsorbed onto the surface of the SnO_2 thin film. Electrons from the surface region of the SnO_2 were 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. The form of the adsorbed oxygen becomes O^- and O_2^- species have been observed. When the thin film of SnO_2 is exposed to a reducing gas like CO, surface reactions such as

$$\mathrm{CO} + O^-_{ads} \rightarrow CO_2 + e^-$$

and 2CO + $O^-_{2,ads} \rightarrow 2CO_2 + 2e^-$ took place. Due to which electrons were released and the electrons released from surface reaction transfer back into the conduction band leading to a decrease in the resistance and an increase in the conductance of SnO_2 thin film.

2.3. Sensitivity test

Sensitivity test was carried out in a closed chamber containing a heating element. Just above the heating element a polished iron slab (sample holder) with a thermocouple was placed. The sample was placed on the sample holder. Two conducting probes were just touched on the sample at extreme ends of the film to measure the resistance at different temperature. Before putting the sample on the sample holder it was heated to 300^0C for 30 minutes to remove water vapors and then cooled to room temperature. Then the resistance of this sample was measured with the help of LCZ meter at different temperatures after injection of carbon monoxide gas concentration of about 50 ppm.

2.4. Optical characterization

Optical characterization was studied from transmission vs. wavelength curve, which was plotted from the data obtained from transmission spectrum analysis of the film by ELCO UV/VIS spectrophotometer Model- SL 159 in the wavelength range 300nm to 1000nm. The refractive index [23] and the thickness [24] of the film were calculated using the envelope method. The formula for refractive index (n) and thickness of the film (d) used in this paper were

$$n = \left\{N + \left(N^2 - \mu^2\right)^{1/2}\right\}^{1/2} \qquad (1)$$

and

$$d = \left| \frac{\lambda_1 \lambda_2}{4(n_1\lambda_2 - n_2\lambda_1)} \right| \qquad (2)$$

Where, N = $2\mu\frac{T_u - T_l}{T_u T_l} + \frac{\mu^2 + 1}{2}$, 'n' refractive index of the thin film, 'μ' refractive index of the material 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, respectively, and 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.

3. Result and Analysis

3.1. Morphology analysis

XRD measurement was carried out by Siemens Diffractometer Model- D 5000 using CuKα having wavelength λ = 0.1540nm radiation with a diffraction angle 10^0 to 70^0. Fig. 1 shows the XRD pattern of SnO_2 thin film deposited on glass substrates. The XRD pattern indicates that a well defined sharp diffraction peaks were obtained nearly at the same angle, 2θ, which may be considered to be the crystalline tetragonal rutile structure of SnO_2 (JCPDS Card No. 88-0287).

The well defined peaks, which match the standard inter-planar spacing JCPDS card no. 88-0287, were given as 26.6^0 for (110) plane, 33.9^0 for (101) plane, 38^0 for (200) plane, 39^0 for (111) plane, 51.8^0 for (211) plane, 54.8^0 for (220), and 61.9^0 for (310) plane.

Since XRD peaks were very narrow and sharp, it shows higher crystalline quality of the SnO_2 film. Since the intensity of (101) plane was more, it may be believed that the preferential growth along direction (101) implies Sn forms an interstial bond with oxygen and exist as rutile SnO_2. The XRD spectra was analyzed with Gaussian function where FWHM was determined. By using the Debye-Scherrer formula

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

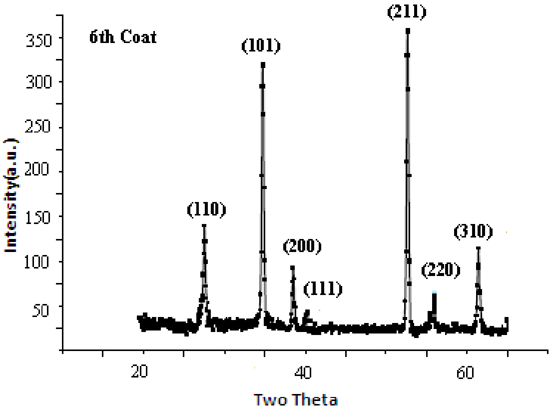

Fig.1: XRD pattern of SnO_2 thin film.

Where, D= Mean grain size, β = FWHM (Full width and half maxima) of the observed peak, λ = wavelength of X-Ray used for diffraction, θ = angle of diffraction. Using the above formula, the average grain size of the deposited film was calculated as 48.54nm.

3.2. Optical analysis

Optical analysis of SnO_2 thin films on glass substrates was studied from transmission percentage vs. wavelength curve in the wavelength range 300nm to 1000nm, which is shown in Fig. 2.

From Fig. 2 it is clear that the surface quality and homogeneity of the thin film were excellent and this confirms that SnO_2 thin film exhibits semiconducting properties as it was established by Nowak that the pure semiconducting compounds have a sharp absorption edge [25]. In the visible region of the spectra, the transmission of SnO_2 thin film was very high due to the fact that the reflectivity is low and there is less absorption due to excitation of electrons from the valence band to conduction band [26].

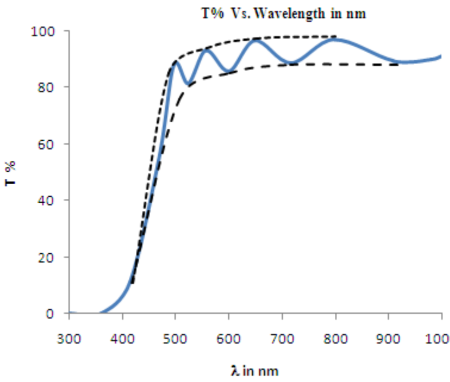

Fig.2: T%Vs. λ in nm in the wavelength range 300nm-1000nm.

From Fig. 2 it may be concluded that the transmittance was more, which may be due to high porosity and larger grain size and less absorption in the film. The lower and upper envelop were used to find out refractive index of the film material and thickness of the film. From the Transmission vs. wavelength data average refractive index and thickness were measured by the above mentioned formulas (1) and (2). The calculated refractive index and thickness of the film were 2.07 and 645.98nm, respectively. The higher value of the refractive index may probably due to high porosity and surface roughness of the films, which is mainly attributed to larger grain size. Sensitivity of thin semiconducting film is highly dependent on film porosity, film thickness, operating temperature, presence of additives, and crystallite size. But porosity is expected to have a large impact on sensor sensitivity. Therefore, in this study we have chosen highly porous thin film.

3.3. Sensitivity analysis

The sensitivity of SnO_2 gas sensor is typically defined as the ratio of the surface resistance (Ra) of the film in air to that in the target gas (Rg) i,e., Sensitivity = $\frac{R_a}{R_g}$. When thin film surface of SnO_2 was exposed to air, due to adsorption the electron depletion layer is formed where electron density is less and thus a layer of high resistance is formed and the adsorbed oxygen remains in the form of O^- and O_2^- species. So the high resistance of SnO_2 thin film is present in air. When the thin film surface of SnO_2 is exposed to a reducing gas like CO due to surface reaction more e^- were released. These released electrons transfer back in to the conduction band, which increase the conductivity or decrease the resistance of SnO_2 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 Fig. 3.

From Fig. 3, it is clear that the maximum sensitivity occurs at temperature of 220^0C. 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. As temperature increases further, more and more adsorb oxygen species reacted and more and more electrons sent back to conduction band leading to increase in conductivity. At 220^0C, which is known as critical temperature T_c , almost all the adsorb oxygen species reacted and maximum electrons sent back to conduction band leading to maximum sensitivity. The decrease in sensitivity for temperatures above a critical operating temperature, T_c , can be attributed to the higher desorption rates at these temperatures. When the target gases are introduced, the added desorption due to the target gases is small relative to the steady-state desorption in air, leading to a decreasing impact on the sensor response for $T> T_c$. Due to competing rates of adsorption and desorption, tin oxide sensors always tend to exhibit a maximum sensitivity at a particular operating temperature, called critical temperature. Generally the operating temperature of the sensor is set as close to critical temperature as possible in order to achieve maximum sensitivity.

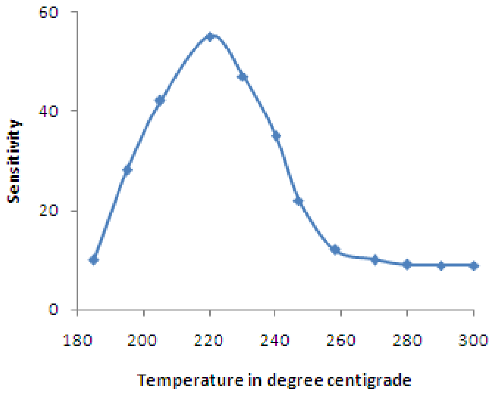

Fig.3: Sensitivity vs. Temperature in ^{0}C.

Fig. 4. shows the relation between the resistance of SnO_2 film in presence of CO gas and the temperature. At low temperature, very small number of adsorbed oxygen species undergoes desorption and very small number of electrons which were released due to this, sent back to the conduction band resulting in high resistance of the film surface. As the temperature increases, a large number of adsorbed oxygen undergoes desorption, and thus resulting more electron in the conduction band, which leads to less resistance of the thin film. At critical temperature, almost all adsorbed oxygen reacts and maximum number of electrons sent back to the conduction band thus resulting minimum resistance of the thin film. Above the critical temperature, the resistance of the film increases,

which may be due to the fact that the added desorption due to the target gases is small relative to the steady-state desorption in air.

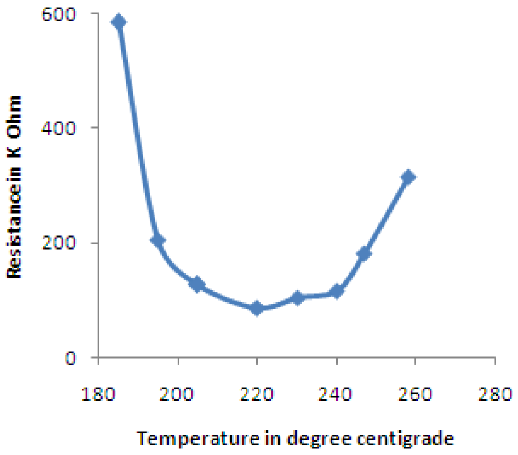

Fig.4: Resistance vs. Temperature in CO gas.

Fig. 5 shows the response time of the thin film at 220^0C i.e., variation of resistance with time. From the figure it is clear that there is a rapid decrease in resistance of about 45K Ohms in 100 second after the injection of CO gas at 50ppm. From the figure, it was concluded that the response time is 20 seconds and the saturation resistance of the film was achieved after 100 seconds, which may be due to the fact that after 100 seconds there will be no adsorb oxygen species left for desorption.

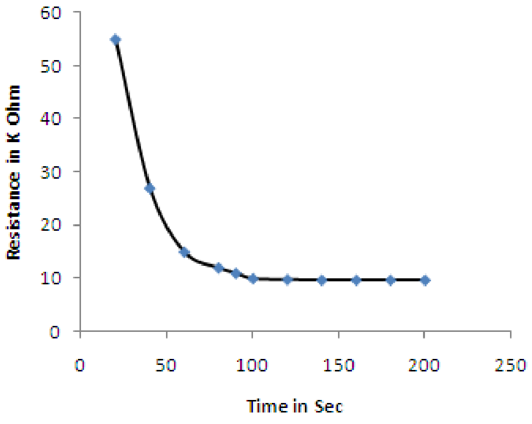

Fig.5: Resistance vs. Time in CO gas.

4. Conclusion

Semiconducting tin oxide thin film was synthesized on glass substrate by Sol-gel dip coating method. From the optical measurement, the thickness of the film was calculated as 645.98nm. XRD study revealed the grain size to be 48.5nm and the product was tetragonal rutile structure. The film was studied for carbon monoxide gas sensing. It was observed that the sensitivity of the film was more at 220^0C to CO gas at concentration 50ppm. Study of response time analysis concluded that the response time was very high i.e., 20 seconds for carbon monoxide gas at 220^0C and concentration of 50ppm. The research is going on to achieve the sensitivity at low temperature.

Acknowledgments

The authors are thankful to Prof. T. S. N. Somayaji, Director of Research (Science & Technology) for providing the Laboratory facility at Nano-Centre, GVP College of Engineering (Autonomous), and for support to carry out the research.

References

[1] A. Sutti, C. Baratto, G. Calestani, C. Dionigi, M. Ferroni, G. Faglia and G. Sberveglieri, Sensors and Actuators B **130**, 567 (2008).

[2] H. J. Lim, D. Y. Lee and Y. J. Oh, Sensors and Actuators A **125**, 405 (2006).

[3] H. L. Qian, K. Wang, Y. Li, H. T. Fang, Q. H. Lu and L. Max, Mater. Chem. Phys. **100**, 82 (2006).

[4] F. F. Ramirez, A. Tarancon, O. Casals, J. Arbiol, A. R. Rodriguez and J. R. Morante, Sensors and Actuators B **121**, 3 (2007).

[5] I. J. Kim, S. D. Han, C. H. Han, J. Gwak, D. U. Hong, D. Jakhar, K. C. Singh and J. S. Wang, Sensors and Actuators B **127**, 44 (2007).

[6] C. Han, D. S. Han, and S. P. Khatkar, Sensors **6**, 492 (2006).

[7] A. M. Ruiz, X. Illa, R. Diaz, A. R. Rodriguez, and J. R. Morante, Sensors and Actuators B **118**, 318 (2006).

[8] L. A. Patil and D. R. Patil, Sensors and Actuators B **120**, 316 (2006).

[9] V. K. Shind, T. P. Gujar, C. D. Lokhande, R. S. Mane and S. H. Han, Sensors and Actuators B **123**, 882 (2007).

[10] E. Comini, G. Faglia, G. Sberveglieri, Z. Pon and Z. L. Wang, Appl. Phys. Lett. **81**, 1869 (2002).

[11] V. S. Vaishnav, P. D. Patel and N. G. Patel, Thin Solid Films **490**, 94 (2005).

[12] P. M. Gorley, V. V. Khomyak, S. V. Bilichuk, I. G. Orletsky, P. P. Hovly and V. O. Grechko, Mater. Sci. and Eng. B **118**, 160 (2005).

[13] R. Mamazza Jr., D. L. Morel and C. S. Ferekider, Thin Solid Films **484**, 26 (2005).

[14] K. S. Yoo, S. H. Park and J. H. Karg, Sensors and Actuators B **180**, 159 (2005).

[15] H. T. Yang and Y. T. Cheung, J. Crystal Growth **56**, 429 (1982).

[16] F. Hui, T. M. Miller, R. M. Magruder and R. A. Weller, J. Appl. Phys. **91**, 6194 (2002).

[17] D. W. Lane, J. A. Coath, K. D. Rogers, B. J. Hunnikin and H. S. Beldon, Thin Solid Films **221**, 262 (1992).

[18] F. Paraguay, D. W. Estrada, L. D. R. Acosta, N. E. Andradeb and M. Miki-Yoshida, Thin Solid Films **350**, 192 (1999).

[19] G. Blandenet, M. Court and Y. Lagarde, Thin Solid Films **77**, 81 (1981).

[20] O. Culha, M. F. Ebeoglugil, I. Birlik, E. Celik and M. Toparli, J. Sol-Gel. Sci. Technol. **51**, 32 (2009).

[21] J. P. Chatelon, C. Tenier, E. Bemstein, R. Berjoan and J. A. Roger, Thin Solid Films **247**, 162 (1994).

[22] B. Oreal, U. Lavrencic-Stangar, Cmjak-Olel, P. Bukovea and M. Kosec, J. Non-Cryst. Solids **167**, 272 (1994).

[23] J. C. Manifacier, J. Gasiot and J. P. Fillard, J. Phys. E: Sci. Instrum. **9**, 1002 (1976).

[24] S. K. Tripathy, P. V. Rajeswary and B. P. Hota, The African Review of Physics **7**, 265 (2012).

[25] M. Nowak, Thin Solid Films **266**, 258 (1995).

[26] K. Y. Rajpure, M. N. Kusumade, M. N. Neumann-Spallart and C. H. Bhosale, J. Mater. Chem. Phys. **64**, 184 (2000).

Received: 29 September, 2012
Accepted: 10 October, 2012