

Cost Effective Experimental Setup for Gas Sensing Applications

Mohammed Afzal¹, P.S.Naik¹, L.I.Nadaf²

¹Department of Physics, Gulbarga University, Gulbarga -585101 Karnataka, India

²Department of Chemistry, SECAB's A.R.S. Inamdar College, Vijayapur- 586101, Karnataka, India

Abstract: In this communication, a simple, cost effective, high temperature gas sensor setup has been designed to measure the gas sensing response of metal oxide thin films. The setup is used to measure gas sensing response of metal oxide thin films at different temperatures ranging from room temperature to about 450 °C. Importance of prepared setup lies in its easy design, compact, reliability, easy way to inject probing gas into the chamber and to carryout temperature dependent gas sensing measurements. It is tested using tin oxide thin films deposited on glass substrate using chemical spray pyrolysis technique and H₂S as the probing gas. It was found to be very sensitive even for a small amount of gas and the recorded gas response to electrical resistance change are quite reproducible. Hence here in it is proposed that the present setup is an innovative design to achieve low cost and high temperature gas sensing device.

Key words: Metal oxide, design and fabrication of gas sensor, tin oxide film, temperature dependent gas response.

I. Introduction

The major applications of gas sensors are domestic or industrial security, environmental and emission monitoring, medical and agribusiness controls, air conditioning in aero planes etc.,[1]. Gas detection has become a concern after the effects of harmful gases on human health were discovered. Many analytical techniques have been developed for sensing different gases. The techniques include electrochemical sensors [3], catalytic sensors [4], Infrared sensor or IR detectors [5], FTIR based sensor [6] Gas sensors using metal oxides that have several advantageous features such as simplicity in device structure, low cost for fabrication, robustness in practical applications and adaptability to wide variety of reductive or oxidative gases. Fairly extensive studies have been carried out on this group of gas sensors. Sensors in the form of thin and thick films based on metal oxide semiconductors like tin oxide are very attractive because of its small size, simple construction, low weight, low power consumption and low cost. Tin oxide (SnO₂) has been extensively studied as gas sensing material for almost half a century. It is found to be sensitive to many gases including reducing gases and oxidizing gases. Gas sensing characteristic of SnO₂ material was proposed by Seiyama et al (7)

The working mechanism of metal oxide sensors is, when metal oxide semiconductors are exposed to oxidizing or reducing gases their resistance vary giving rise to a large and reversible signal. The detection process is known to be based on the reversible adsorption/desorption phenomena at the surface. This change in electrical conductivity is due to the adsorption of gaseous species on the surface atoms of film by a chemical reaction. The metal oxide causes the gas to dissociate into charged ions or complexes on the surface, which results in the transfer of electrons from film to gas molecules or vice versa. This property has been exploited for the detection of toxic gases.

At present the research on these gas sensors is aimed at obtaining new materials to achieve high sensitivity, a good stability and a long operating life [10]. In the present communication an innovative gas sensor setup has been designed and fabricated as low cost, reliable and method to carry out the gas sensing measurements at high temperature. The present setup is tested well for tin oxide (SnO₂) films with respect to Hydrogen Sulphide (H₂S) gas

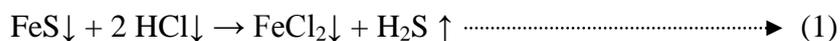
II. Experimental technique

All the chemicals used for the synthesis of SnO₂ thin films were of analytical grade and were used without further purification. Stannous chloride SnCl₄.5H₂O used as the precursor that was obtained from Thomas Beker, India. Ethanol (C₂H₅OH) was used as the solvent for all the synthesis and is obtained from sd-fine chemicals, India. Our home made chemical spray pyrolysis setup is used for the synthesis of SnO₂ films. Here the spraying system consists of spray nozzle, air compressor and mechanical arrangement for one dimensional motion. And heating unit consists of a hot plate, thermocouple, temperature indicator and variac. Spray nozzle and hot plate with glass substrate are housed in a metallic box and the out let of the box is fitted with an exhaust fan to remove the toxic gases produced during the decomposition of spray solution. In a typical synthesis of these films, SnCl₄.5H₂O was dissolved in ethanol and stirred well for a long time and filtered using filter paper to get a clear solution. Here 0.2 M solution of SnCl₄.5H₂O was prepared in 20 ml of ethanol. The

commercial laboratory glass slides of dimensions 25 mm x75 mm and thickness 1mm were used as substrates to deposit films. The slides were washed with de-ionized water, rinsed in ethanol and dried and placed in laboratory oven at temperature approximately 50°C. The prepared 20 ml solution was sprayed on a preheated glass substrate. The temperature of the substrate was maintained at a constant value of 400°C with ±1°C by using variac and digital temperature controller. The nozzle to substrate distance was kept constant at 35 cm. The entire solution was sprayed in about 8-10 minutes. For the uniform deposition of the solution the substrate is kept stationary while the nozzle is made to move to and fro on a line with a programmed stepper motor using micro controller, where the program is such that one can set the speed of nozzle motion and the number of cycles to be repeated during the deposition. Once the spray is completed the heater was turned off and the SnO₂ films were allowed to attain the room temperature by naturally cooling.

The as prepared SnO₂ films were used for further characterization. X-ray diffractometer (Ultima IV Japan) with CuK_α radiation (λ=1.5405 Å) at 40 mA and 40 kV at a scanning rate of 0.02° per second was used to study the crystal state of these films. Optical properties of the films were studied using UV-VIS spectrometer (Specord- 200 plus Germany) in the wavelength region 200 – 1100 nm. The surface morphology of the films was studied using Scanning Electron Microscope. And the elemental composition was studied using EDAX spectrum. The current-voltage (I-V) characteristics of the films were studied using programmed Keithley source meter (Keithley 2636A). The sensing behavior of the films in terms of variation in the resistance was studied using digital multimeter and the temperature of the micro heater by digital thermometer using alomel- chromel thermocouple.

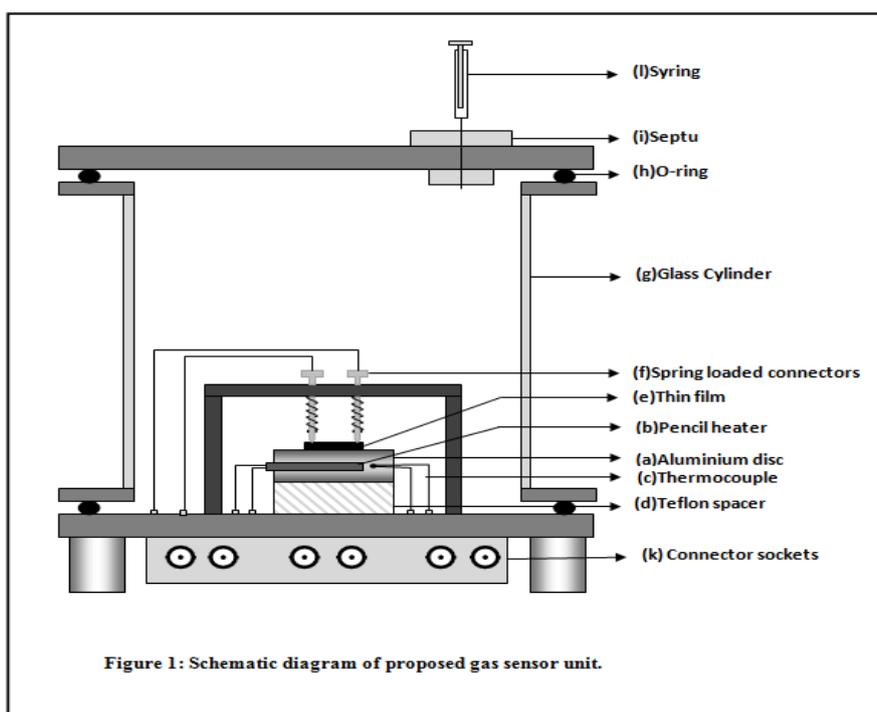
In order to use SnO₂ for gas sensing application, as prepared SnO₂ films were cut into small piece having width 2 mm and length 6 mm. These films were washed with de-ionized water and rinsed in boiling trichloroethylene (C₂HCl₃) solution to degrease them. The film was loaded on the heating element in the gas sensor unit and conductivity was measured using the spring loaded contact of the present setup. To test the workability of the sensing element H₂S gas was used. It was generated using FeS and dilute HCl in a sealed container. The chemical reaction is given below as equation (1)



III. Results and Discussion

3.1 Experimental setup

The schematic diagram of our gas sensor setup unit is shown in figure (1) and its photograph is shown in fig (2). A circular Aluminum disc of diameter 32 mm and thickness 11mm. (a) with a pencil heater (b) of 12W embedded in it is used as a heating element for localized heating of the



Film. One junction of thermocouple (c) using Alumol Chromel is fixed in contact with the heating element for temperature measurements. Below this a Teflon spacer (d) of diameter 32 mm and thickness 9 mm is provided for thermal insulation. Above the heating element, SnO₂ thin film sample of size 2mm x 6mm is mounted as gas sensing element (e). Two spring loaded connectors (f) are provided for electrical connection for the resistance measurements.



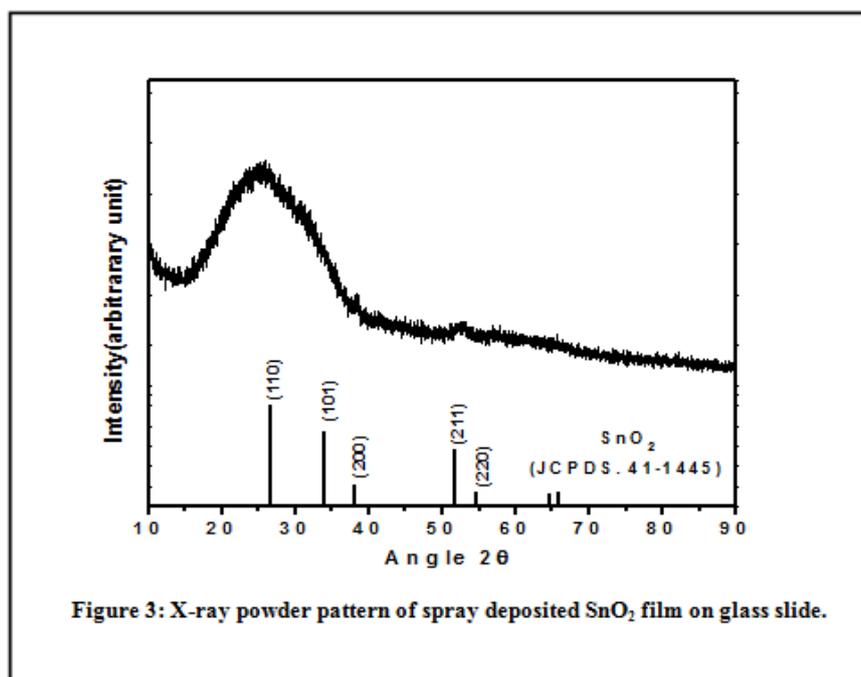
Figure 2: Photograph of the proposed gas sensor setup.

This assembly is housed in a glass cylinder of diameter 110 mm and length 115 mm (g) with one annular aluminum disc attached on either side of the glass cylinder. A flange coupling using O ring (h) with circular Aluminum discs either side (one top and one bottom) is used for air tight compartment. All electrical connections are drawn through the bottom plate. In the top plate (lid) a septum (i) is provided to inject the gas into the chamber using a syringe. A cork (j) is used to let the dry air into the chamber and expose the films to air. This entire assembly is mounted on a wooden base fixed with a panel of six connector sockets (k); two for resistance measurements, two for applying voltage to the heater and two for temperature measurements. A syringe (l) is used to inject the gas into the chamber. A d.c power supply 0-30V and 5 A is used for applying voltage to the heater; a temperature indicator is used for temperature measurements. And a digital multimeter is used for resistance measurements.

The gas response in terms of the variation in resistance when exposed to gas at different temperatures is recorded. H₂S gas is used to test the performance of the gas sensor unit. Every time a known amount of H₂S gas is injected into the chamber and the variation in the resistance of the thin film is recorded as a function of time. It is found that there is decrease in resistance of the sensing element in presence of H₂S gas. When the H₂S gas is injected into the unit, the resistance of the element decreases rapidly and reaches a constant value in a short course of time. When the element is exposed to air by opening the cork and allowing the air to enter the chamber, the resistance of the element increases and reaches its initial value. The decrease in resistance with respect to time is recorded when exposed to H₂S gas and the increase in resistance with respect to time is recorded when exposed to open air. This procedure is repeated for several time and obtained reproducibility curves are discussed further in this section.

The as deposited SnO₂ films using chemical spray pyrolysis were uniform and almost transparent on glass slide. Already there are several techniques to synthesize SnO₂ thin films, such as aerosol technique [11], controlled solid – vapor process [12], laser ablation technique [13], wet chemical route [13], thermal evaporation [14] etc. However among all the available techniques the chemical spray pyrolysis is one of the simple, versatile and easy technique that does not require vacuum and other special accessories. Moreover it gives good quality films with uniform thickness [15, 16].

The films were used for X-ray analysis, the recorded powder diffraction pattern is shown in figure (3). The peaks are observed at $2\theta = 26.61^\circ, 33.89^\circ, 37.95^\circ, 51.78^\circ$ and 54.75° corresponds



to the Miller indices (110), (101), (200), (211) and (220) respectively. This reveals that the observed peaks are comparable to the characteristic peaks of tetragonal phase of SnO₂ (JCPDS Card No. 41-1445). The broad peak in the XRD pattern indicates that the prepared SnO₂ films are having small particle size. So the small size of the particles would lead to high surface to volume ratio leading to high density of surface atoms and hence can be a useful material for gas sensing applications. From the pattern, the average crystallite size is estimated using Debye Scherer formula $d = k \lambda / \beta \cos \theta$ where k is shape factor which has value about 0.9, λ is the X ray wave length, β is the full width half maxima (fwhm) and θ is the Bragg angle. The particle size is estimated from fwhm of broad peak is found to be less than 5 nm and θ . And the particle size is found to be less than 5 nm. There are many reports on the chemical spray by others of SnO₂ film due to the potential application in various areas. **Th. Becker** et al. have reported the grain size of SnO₂ films to be 50 nm, [17] U Nerle et al. have reported the crystallite size of SnO₂ film deposited using spray technique is about 50 nm to 70 nm [18]. Soumen Das et al have reported the diameter of the nano particles to be 10 nm [19]. In the present study the XRD peak is broad which indicate the small size of the particles the size of the particle. This gives large density of surface dangling bonds on the surface of film, which is more suited for gas sensing applications that helps in obtaining the improved gas sensitivity of a material.

The films were used to study the optical absorbance and transmittance in the wavelength region from 200-1100 nm, a typical curve is shown in figure (4). The absorption curve shows its optical gap transition close to 350 nm which corresponds to the optical band gap (E_g) of about 3.5 eV Figure (5) shows the transmittance behavior of the same film. It is observed that the films have highest transmittance that is close to 80%. T Serin et al have carried out optical absorption studies and reported optical band gap of SnO₂ films in the range 3.94-3.96 eV [17]. In the present work absorption curve of intrinsic SnO₂ shows its optical gap transition close to 350 nm corresponding to the band gap (E_g) equal to 3.5 eV, similar results were reported by U Nerle et al. and it has almost flat base prior to absorption edge [17].

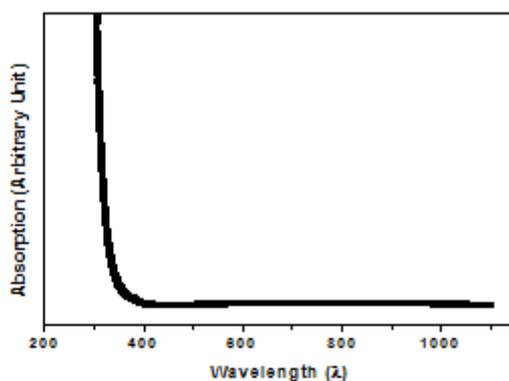


Figure 4: Optical absorption of SnO₂ thin film recorded between 300 nm to 1100 nm.

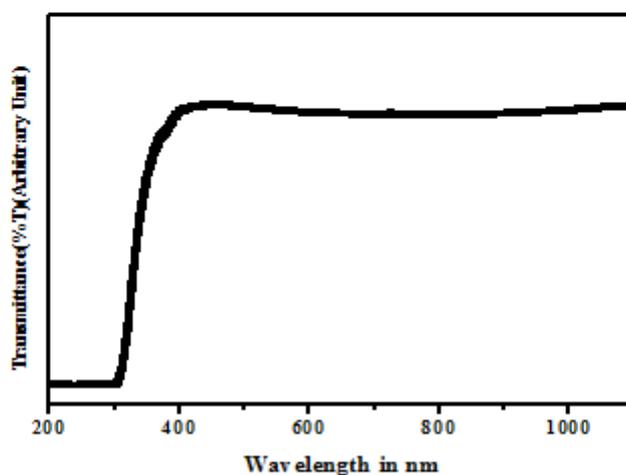
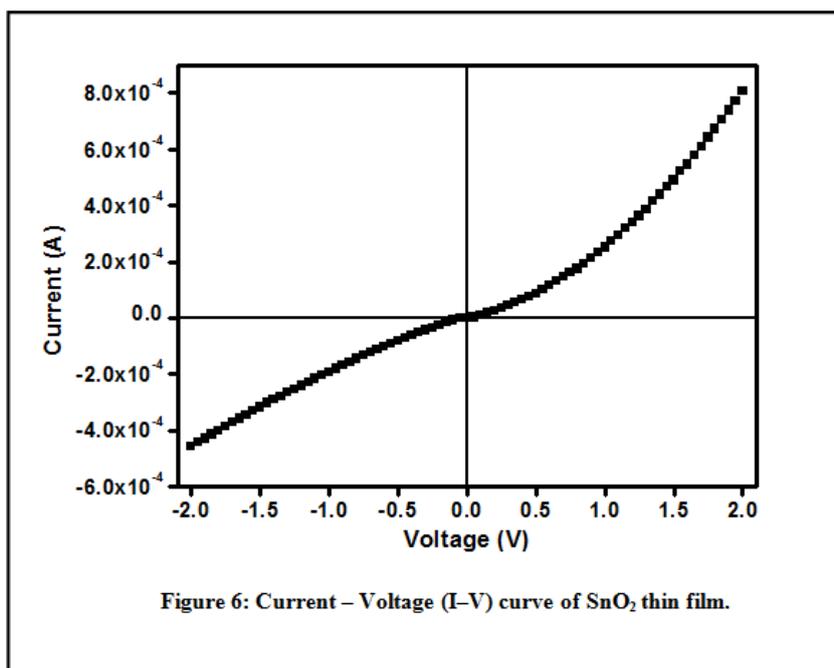
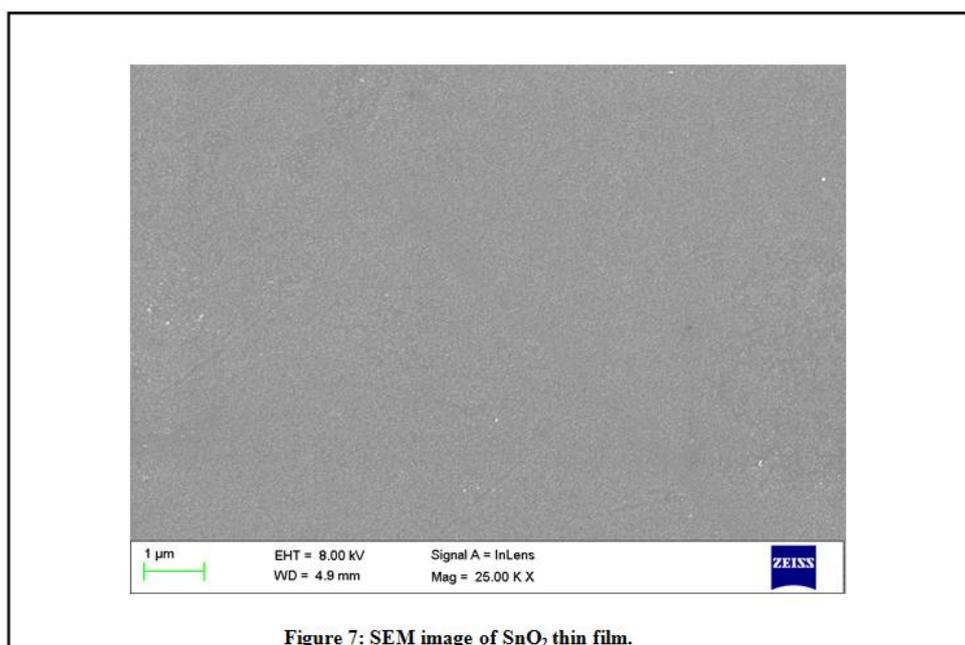


Figure 5: Optical transmittance spectrum of SnO₂ thin film of glass slide.

Further, the electrical conductivity is measured by measuring current voltage curve of these films in two probe configuration. Figure (6) shows the I-V characteristics of the SnO₂ thin film. The curve shows the pseudo ohmic behavior. From the slope of the curve the electrical resistance is estimated that is about 3 kΩ.



The surface morphology of SnO₂ thin film was studied using a scanning electron microscope. The films exhibit uniform and granular morphology covering entire substrate area. The SEM image of film is shown in figure (7). The elemental composition is obtained from the EDAX spectrum showed the presence of tin and oxygen. In addition to tin and oxygen silicon was also detected. The appearance of silicon in the EDAX spectrum is because of the glass substrate used for deposition of the film. EDAX spectrum is shown in the fig (8)



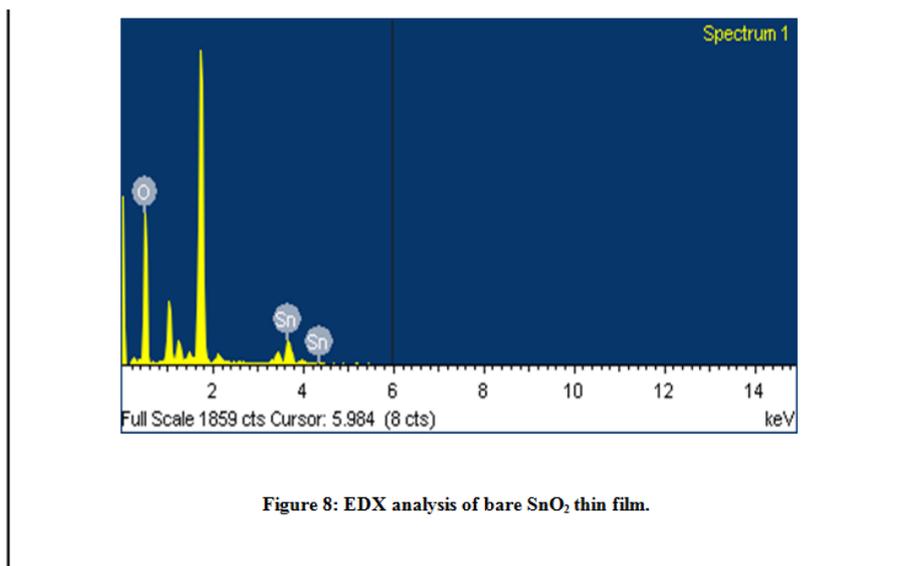


Figure 8: EDX analysis of bare SnO₂ thin film.

The gas sensing characteristics of thin film of SnO₂ were investigated. Sensitivity S is defined as the ratio of effective change in resistance for the test gas to the original value of the resistance in air. It is given by $S = \frac{(R_o - R_g)}{R_o} \times 100\%$. Where R_g is the sensor resistance in the presence of the test gas and R_o is the sensor resistance in dry air, measured at that temperature. The temperature of the heating element was set in the range from room temperature to about 450⁰ C. Gas sensing measurement was carried out at different temperatures.

A known amount of H₂S gas is injected into the chamber using syringe through the septum. The fall in resistance of the sensor with respect to time is recorded. When once the minimum constant resistance value is reached the the sensor is exposed to open air. Now the increase in the resistance with respect to time is recorded. Similar procedure was repeated for several times and it is observed that the recorded behavior is quite reproducible. Figure (8) shows the sensing characteristics of SnO₂ thin film measured at 250° C and 350° C when exposed to a fixed amount of H₂S gas. Upon exposure to the H₂S gas the film resistance is seen to decrease. From the sensing characteristics it is found that the response time is less, where as the recovery time is slightly more. The reproducibility is very good. G Patil et al. have tested SnO₂ thin films for various gases at different operating temperatures ranging from 50°C to 450°C and found the SnO₂ films deposited by spray technique shown maximum sensitivity to H₂S gas at 100°C [19] . Comparison of gas sensing characteristics of SnO₂ based gas sensors by others [20] (nanofibres, nanocrystals, thin films, submicrotubes, etc) to H₂S for different concentration is made and established that SnO₂ thin films show maximum response to H₂S at an operating temperature of 100°C for 80 ppm. In present study we have recorded the gas sensor response using our setup to sense H₂S gas at 250°C, 350°C and the sensor response curves are shown in figure (9)

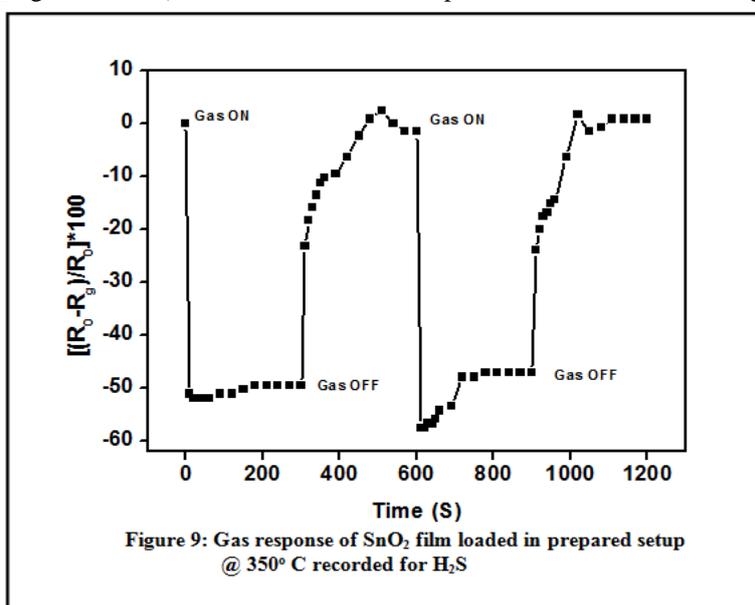


Figure 9: Gas response of SnO₂ film loaded in prepared setup @ 350° C recorded for H₂S

IV. Conclusions

The setup has been proposed to measure the gas response of different gases in terms of variation in electrical resistance of sensing element. It is quite simple, cost effective, reliable and sensitive to detect H₂S gas. The setup is able to measure sensing property of the samples at different temperatures. The workability of the present setup is clearly shown in the gas response characteristic curve, which is electrical resistance verses time. The present setup has been used successfully to study the sensing property of SnO₂ films of nano grain size for H₂S gas. It can be easily extended to the other sensing materials and also for other gases of interest.

Acknowledgments

Facilities developed at SECAB A.R.S. Inamdar College for women, Vijayapur under the financial assistance by the University Grants Commission (UGC), Govt of India, under the Scheme CPE and Minor Research Project to Mohammed Afzal have been used. The authors would like to thank UGC and ARSI College.

References

- [1]. Xiao Liu, Sitian Cheng, Hong Liu, Sha Hu, Daqiang Zhang and Huansheng, A survey on Gas sensing Technology, Sensors 2012,12 9635-9665
- [2]. G Eranna, Metal oxide nanostructures for gas sensing device Chapter 1, CRC press Taylor & Fransis group
- [3]. E Bakker, Electrochemical sensors, Anal. Chem 2004 76(12) pp 3285-3298 ACS pub.
- [4]. E Allan Symons, Gas sensors 1992 pp 169-185
- [5]. Thomas Topfer, Konstantin P. Petrov, Yasuharu Mine, Dieter Jundt, Robert F. Curl and Frank K. Tittel, Room-temperature mid-infrared laser sensor for trace gas detection, Applied Optics, Vol, 36 pp. 8042 – 8049 (1997)
- [6]. S.Lenaert, J Roggen, G Maes ; FT-IR Characterization of Tin Oxide gas sensor material Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy Vol, 51 issue 5 May 1995 pp 883 – 894
- [7]. T.Seiyama, A. Kato, K Fujiishi, M. Nagatani. A new detector for gaseous components using semiconductive thin film, Anal. Chem. 34 (1962) 1502-1503]
- [8]. G. Eranna, B.C Joshi, D.P.Runthala and R.P.Gupta Oxide materials for Development of Integrated Gas Sensors – A comprehensive Review; Critical Reviews in Solid State and Materials Science, 29, 111-188, 2004
- [9]. Noboru Yamazoe: New approaches for improving semiconductor gas sensor: Sensors and Actuators B Chemical Volume 5 Issue 1-4 August 1991 pp 7-19
- [10]. Chengxiang Wang, Longwei Yin, Luyuan Zhang, Dong Xiang and Rui Gao: Metal Oxide Gas Sensors: Sensitivity and Influencing Factors ; Sensors 2010, 10 (3) 2088-2106
- [11]. G.Korotsenkov Metal Oxides for Solid State Gas Sensors : What determines our choice; Materials Science and Engineering: B Volume 139, Issue 1, 25 April 2007 pages 1-23
- [12]. Yuri T. Didenko and Kenneth S.Suslick Chemical Aerosol Flow Synthesis of Semiconductor Nanoparticles ; J Am. Chem. Soc., 2005, 127 (35), pp 12196-12197
- [13]. Kurt W, Kolasinski;Catalytic growth of nanowires: Vapour-liquid- solid, vapour-solid-solid, solution-liquid-solid and solid-liquid-solid growth ; Current Opinion in Solid State and Materials Science Volume 10, Issue 3-4 August 2006, Pages 182-191
- [14]. Geraint Williams and Gary S.V Coles ; The Gas sensing potential of nanocrystalline Tin Oxid produced by Laser Ablation technique MRS Bulletin/Volume 24/Issue -06/June 1991/ pp -25-29
- [15]. Z R Dai, Z.W.Pan and Z.L.Wang ; Novel Nanostructures of Functional Oxides Synthesized by Thermal Evaporation ; Advanced Functional materials volume 13 Issue -1 pages 9-24 January 2003
- [16]. P.S.Patil, Varsatility of spray pyrolysis technique, Material Chemistry and Physics, 59, 185-198 (1999)
- [17]. Bhavan Godbole, Nitu Badera, S.B.Shrivastav and V.Ganesan – A simple chemical spray pyrolysis apparatus for thin film preparation. JI of Instrum. Soc. of India. Vol 39 No 1 March 2009
- [18]. T. Serin, N. Serin, S Karadeniz, H Sari, N. Tugluoglu, O. Pakma : Electrical, Structural and Optical properties of SnO₂ thin films prepared by spray pyrolysis Journal of Non-crystalline solids 352 (2006) 209-215
- [19]. Uma Nerle, R.M.Hodlur and M.K.Rabinal : A sharp and visible range plasmonic in heavily doped metal oxide films: Material Research Express 192014) 015910
- [20]. Ganesh E Patil, D D Kajale, D N Chavan, N K Pawar, P T Ahire, S D Shinde, Synthesis, Characterization and gas sensing performance of SnO₂ thin films prepared by spray pyrolysis, Bull. Mater. Sci., Vol. 34 No. 1 February 2011, pp 1-9 _ c Indian Academy of Sciences.
- [21]. Lin Mei, Yuejiao Chen and Jianmin Ma, Gas Sensing of SnO₂ Nanocrystals Revisited: Developing Ultra-Sensitive sensors for Detecting the H₂S Leakage of Biogas, Scientific Reports 4:6028