Synthesis and Study of Electrical Properties of Di Ethylene Glycol Embedded ZrO_2 Films as a Gas Sensor

P.S. More[1,*], Y.B. Khollam[2] and S.G. Gawande[1]

[1]*Department of Physics, Novel Material Characterization Laboratory, Government Institute of Science, Mumbai 400 032 (MS), India*

[2]*Department of Physics, Anantrao Pawar College, Pirangut, Tal.-Mulshi, Dist.-Pune, Pune 412 115 (MS), India*

Abstract: In this paper, the effect of Di ethylene glycol (DEG) embedded zirconium dioxide (ZrO_2) on microstructure and liquid petroleum gas (LPG) sensing characteristics of ZrO_2 thin films prepared by spray pyrolysis method were investigated. The films are prepared at X wt. % concentrations (X = 1, 2, 3, 4 and 5) of DEG. Microstructure of ZrO_2 thin film was drastically changed by the addition of DEG, indicating that the addition of DEG was effective to prevent the agglomeration of ZrO_2 particles. The high material and phase purities are found from the characterization studies in all as-prepared films. The better sensitivity factor (SF) values SF ~102 (at T = 45^{0}C) and SF = 100 (at T = 37^{0}C) are obtained at 1 wt. % and 5 wt. % of DEG respectively. It is observed that the gas sensing characteristics of these films are strongly influenced by the optimum concentration of DEG due to the high surface area of nano-sized ZrO_2 particles.

Keywords: DEG, Spray pyrolysis, LPG, Gas sensor, thin film.

1. INTRODUCTION

Now a days, the increase in ecological perception, fitness, and safety are involving the greenhouse, inflammable and poisonous gases. As a result, there is an urge of reliable and contemptible gas sensors [1-12] to control the emission of gases. Polymer embedded metal oxide semiconductor is the most widely used to detect oxidizing gases and it also prevents from atmospheric wetness. Moreover, there are new approaches to improve the metal oxide semiconductor sensors by modifying the surface morphology with the help of polymer [10-13].

In this present work, we have synthesized the DEG embedded ZrO_2 film using the spray technique. An organic structure-directing agent is used in this synthesis process. The samples obtained from above mentioned process were heated up-to a particular temperature 100^{o}C. In this study, effect of DEG addition on the microstructure and sensor characteristics of ZrO_2 thin film was investigated.

2. EXPERIMENTATION

Standard commercially available zirconium oxy-chloride (99.8 % pure, SISCO RESARCH PVT. LTD.) and pure Di ethylene glycol (DEG) (S.D. Fine chime Ltd.) were used to prepare the thin films. Initially, 1 molar solution of DEG and zirconium oxy-chloride was prepared. DEG content was varied from 0 to 5 wt. % of precursor solution. Then the thin films of each of concentration were prepared by spray pyrolysis method on glass slides, which were used as substrates. ZrO_2 thin films were deposited on glass substrates by spray pyrolysis method, followed by baking at 100 ^{o}C in air ambient immediately. Sensing properties were studied for all the films for LPG by recording the change in the voltage across the sample by half bridge method. The sensor characteristic was evaluated by the electrical conductivity of thin films between electrodes in the temperature range of 30-100 ^{o}C. The sensitivity factor (SF) of the sensor was defined as $(R_g/R_a)*100$, where, R_a is resistance in air, and R_g resistance in LPG gas at 1000 ppm concentration.

3. RESULTS AND DISCUSSION

Sensor study: As already reported, the gas sensitivity was almost linear to the concentration of LPG at 1000 ppm from room temperature to 100°C for the ZrO_2 based device. The gas sensitivity is defined as the ratio of resistance of sample in gas surroundings ($|R|_{gas}$) to its resistance in air ($|R|_{air}$). The sensor study is optimized for following condition (i) temperature selectivity and (ii) weight concentration.

3.1. Temperature Selectivity

Figure **1** shows the variation of sensitivity factor with respective optimum operating temperature for different weight concentration of DEG. It can be seen that for 1 wt. % sample, the sensitivity up to 37°C is almost constant and increases rapidly at 45°C and further decreases up to 57°C and then again remains

*Address corresponding to this author at the Department of Physics, Novel Material Characterization Laboratory, Government Institute of Science, Mumbai 400 032 (MS), India; Tel: +91 09422759961; Fax: +91-022-22047962;
E-mail: p_smore@yahoo.co.in

E-ISSN: 1929-5995/12

constant. The flat response is obtained for the 2, 3, and 4 wt. % of DEG modified samples at all the temperatures between 30 and 100°C.

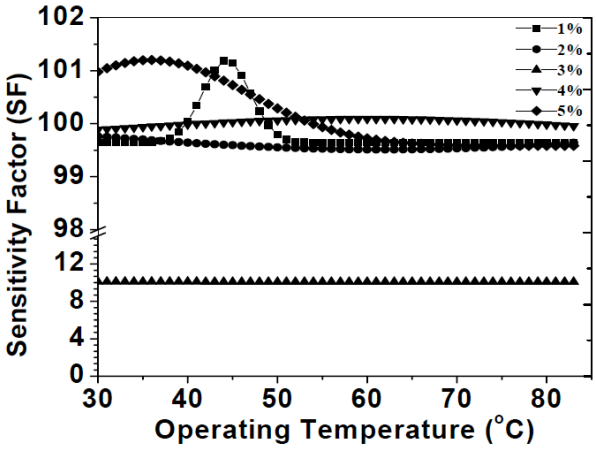


Figure 1: Variation of SF (sensitivity factor) with temperature for LPG gas (1000 ppm) at (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5, wt.% of DEG for DEG /ZrO_2 system.

However, it has shown that the sensitivity to 5 wt. % sample (SF~102) increases continuously up to 37°C and decreases further to 100°C. The sensitivity is noticeable at low temperature, but the temperature window for 1 wt. % sample is less as compared 5 wt. % sample. These results are summarized in Table **1**. The response and recovery reactions are found to be fast.

3.2. Optimization of Weight Concentration

From Figure **2a** it reveals that 1 wt. % DEG modified sample gives more sensitivity (SF = 101. 20) at 47°C as compared to 2, 3, 4 wt. % DEG modified samples.

While, 5 wt. % DEG modified sample (Figure **2b**) gives less sensitivity (SF= 101.18) at 37°C. Further investigation like XRD, SEM and activity of LPG on the sensor study is now in progress. It seems that both adsorption and combustion of the reducing gases occurs on the surface of the sensors. The depletion of the lattice oxygen might be responsible for the sensitivity of the sensor to the gases. The ZrO_2 is a lower temperature semiconductor than other oxides and exchanges lattice oxygen with surface and gas-phase oxygen more easily [5, 11]. We speculate that at 35°C, the LPG can easily extract more oxygen from the lattice of the sensor. Thus, in ZrO_2 sensor the lattice oxygen is easily replaced from the gas and causes the change in resistance/conductivity of sample.

Yamazoe and Miura [7] reported that the sensitivity was drastically developed by decrease in the crystalline size to a few nano-meters (crystallite size effect). In addition, it was reported that the thin film thickness under a micron-meter and addition that the improvement of sensitivity of ZrO_2 thin film was brought by high surface area of nanosized ZrO_2 particles and high oxygen defect concentration caused by the combustion of organic chemical modifier reagent (DEG) was effective to enhance the sensitivity of the sensors [12,13]. In our results, the addition of DEG was so effective to decrease the particle size of the ZrO_2 thin films that sensitivity of the ZrO_2 thin film could drastically be enhanced. The atmospheric oxygen adsorbs on the surface by extracting an electron from conduction band, in the form of super oxides or peroxides, which are mainly responsible for detection of the test gases. At higher temperature it captures the electrons from conduction bands as

$$O_2 \text{ (air)} + 4\ e^- \text{ (conduction band)} \rightarrow 2O^{2-} \text{ (film surface)}$$

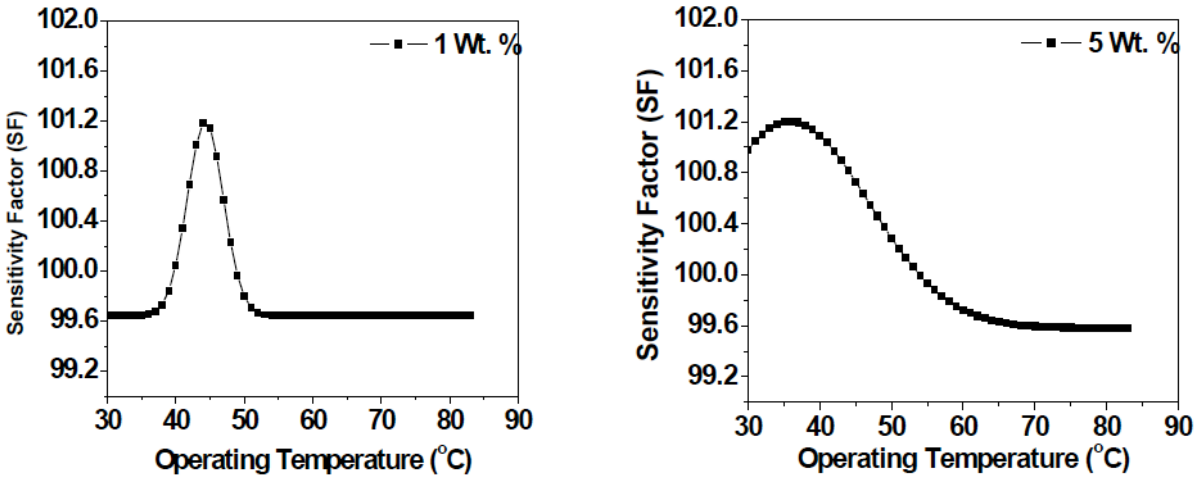
It would result in decrease in conductivity of the samples. When LPG reacts with the adsorbed oxygen on the surface of the sample it get oxidizes to CO_2 and H_2O, liberates free electrons in the conduction bands. The reaction that takes place is as

$$C_4H_{10\ (gas)} + 13O^{2-}_{\ (film\ surface)} \rightarrow 4CO_{2\ (gas)} + 5H_2O_{\ (gas)} + 26\ e^-_{\ (conduction\ band)}$$

This shows the n-type conduction mechanism. Thus generated electron contributes to sudden increase in conductivity of the sample. As the temperature is increased, the ZrO_2 can exchange lattice oxygen with surface and the gas. The study of dramatic effect of

Table 1: Variation of Weight Concentration with Respective Optimum Operating Temperature °C.

additive Weight %	Maximum sensitivity	Optimum operating Temp.	Temperature window in °C
1	101.20	45°C	4
2	97	-	NIL
3	10	-	NIL
4	99	-	NIL
5	101.18	37°C	10



(a) **(b)**

Figure 2: Variation of SF with operating temperature for LPG gas (1000 ppm) at (**a**) 1, and (**b**) 5 wt.% of DEG in Di ethylene Glycol/ZrO_2 system.

zirconium on LPG selectivity needs further investigation.

4. CONCLUSION

The DEG embedded ZrO_2 films used in gas sensors have received great attention. The high and selective absorption properties of DEG embedded ZrO_2 films towards a specific gas greatly enhances the sensing selectivity for the gas. The compound or cluster sensing towards a gas assembled into the cages or channels of DEG embedded ZrO_2 results in its high stability, and maximally elevate the sensing property of the materials. The applications of composite materials partially composed of a DEG open novel ways for choosing gas sensor materials as well. However, much more work remains to be done. Overall, we foresee that DEG embedded ZrO_2 will become widely available material for gas sensing in the next few years.

REFERENCES

[1] Fuller MJ, Warwick ME. The catalytic oxidation of carbon monoxide on tin (iv) oxide. J Catal 1973; 29: 441-50. http://dx.doi.org/10.1016/0021-9517(73)90251-0

[2] Tatsuyama CH. Ichimuraand SH. Iwakuro H. Observation of GaSe–SnO_2 heterostructure by XPS and AES. Jpn J Appl Phys 1982; 21: L25-L27. http://dx.doi.org/10.1143/JJAP.21.L25

[3] Chaudhary VA, Mulla IS, Sainkar SR, Belhekar AA, Vijayamohanan K. Surface ruthenated tin oxide as a novel hydrocarbon sensor. Sensors & Actuators A 1988; 65: 197-202. http://dx.doi.org/10.1016/S0924-4247(97)01688-9

[4] Duh JG, Jou JW, Chiou BS. Catalytic and gas sensing characteristics in Pd doped SnO_2. J Electrochem Soc 1989; 136: 2740-47. http://dx.doi.org/10.1149/1.2097581

[5] Ippommatsu M, Sasaki H, Yanagida H. Sensing mechanism of SnO_2 gas sensors. J Mater Sci 1990; 25: 259-62. http://dx.doi.org/10.1007/BF00544217

[6] Yamazoe N. New approaches for improving semiconductor gas sensors Sensors & Actuators B 1991; 5: 57-19. http://dx.doi.org/10.1016/0925-4005(91)80213-4

[7] Yamazoe N, Miura N. In: Yamauchi S, Ed. Chemical Sensor Technology, Kodansha/Elsevier, New York 1992; vol. 4: pp. 19-42.

[8] Ruu AR, Seshdrj K, Rao CNR. Investigations of V_2O_5 based LPG sensors Talonto 1992; Vol. 39/11: pp. 1543-1547.

[9] Orlik DR, Ivanovskaya MI, Kol KD. Characterization of semiconducting tin oxide films sensors prepared by sol–gel method. J Anal Chem 1995; 50: 1073-77.

[10] Schweizer B, Berberich M, Zheng JG, Weimar U, Goepel W, Barsan N, *et al.* The effect of Pt and Pd doping on the response of nanocrystalline SnO_2 gas sensors to CO, Sensors & Actuators B 1996; 31: 71-75. http://dx.doi.org/10.1016/0925-4005(96)80018-9

[11] Chaudhary VA, Mulla IS, Vijayamohanan K. Synergistic sensitivity effects in surface modified tin oxide using Ru–Pd oxides. J Mater Sci Lett 1997; 16: 1819-21. http://dx.doi.org/10.1023/A:1018568702315

[12] Shimizu Y. Development of high performance semiconductor gas sensors by micro- and macro-structural design. Chem Sensors 2002; 18: 42-54.

[13] Shoyama M, Hashimoto N. Effect of poly ethylene glycol addition on the microstructure and sensor characteristics of SnO_2 thin films prepared by sol–gel method. Sensors & Actuators B 2003; 93: 585-89. http://dx.doi.org/10.1016/S0925-4005(03)00215-6

Received on 16-10-2012 Accepted on 02-12-2012 Published on 31-12-2012

DOI: http://dx.doi.org/10.6000/1929-5995.2012.01.02.2