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

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Abstract: In this paper, the effects of Di ethylene glycol (DEG) embedded Zirconium dioxide (ZrO_2) 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 Di ethylene Glycol. 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^{o}C) are obtained at 1 wt. % and 5 wt. % of Di ethylene Glycol 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 ZrO2 particles

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

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 Di ethylene Glycol and Zirconium Oxichloride was prepared. PEG 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 is used as substrate. ZrO_2 thin films were deposited on glass substrate 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 ($|R|_{gas}$) surroundings and its resistance in air i.e. ($|R|_{air}$). The sensor study is optimized for following condition (i) Temperature Selectivity (ii) optimization of 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 increase rapidly at 45°C and further

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decrease up to 57°C and then again remains constant. The flat response is obtained for the samples of 2, 3, and 4 wt. % of DEG modified samples at all the temperatures range from 30-100° C.

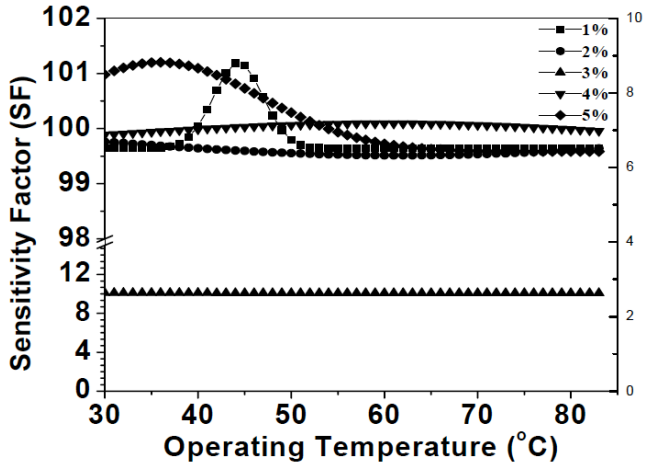


Figure 1: Variation of SF (sensitivity factor) with temperature for LPG gas (1000 ppm) at (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5, wt.% of DEG for DEG /ZrO_2 system.

However, it has shown that the sensitivity to 5 wt. % sample (SF~102) increase continuously up to 37°C and decrease further to 100°C, even sensitivity noticeable at low temperature, but the temperature window for 1 wt. % samples is less as compared 5wt% sample are summarized in Table **1**. The response and recovery responses were rather quick.

3.2. Optimization of Weight Concentration

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

While, 5 Wt. % Di ethylene Glycol 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 PEG was so effective to decrease the particle size of the SnO2 thin films that sensitivity of the SnO2 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

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

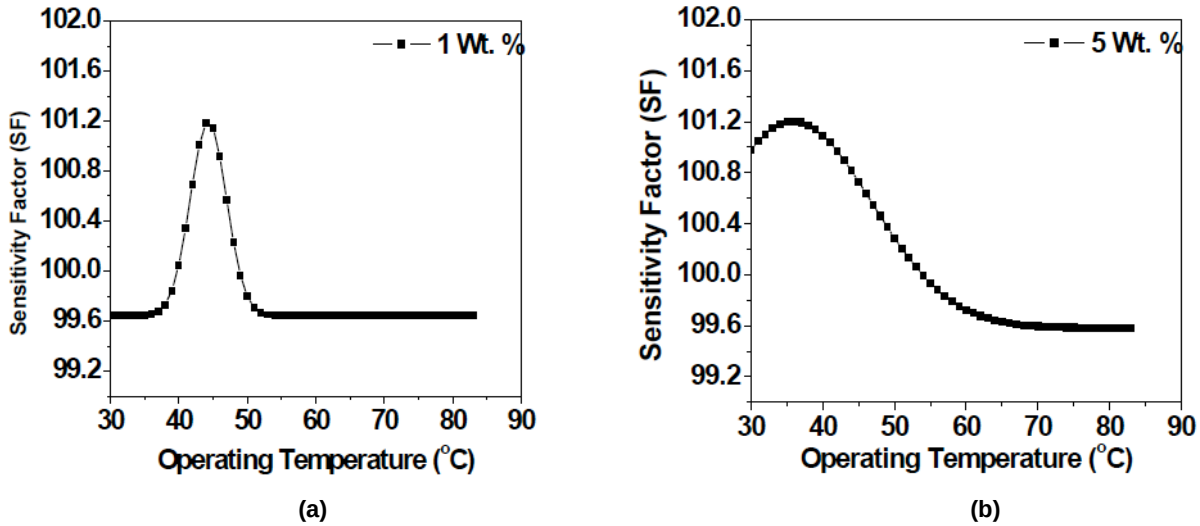
It would result in decrease in conductivity of the samples. When LPG reacts with the adsorbed oxygen on the surface of the samples it get oxidizes to CO_2 and H_2O, liberate free electrons in the conduction bands. The reaction that takes place is as

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

This shows the n-type conduction mechanism. Thus generated electron contributes to sudden increase in

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 temperature for LPG gas (1000 ppm) at (**a**) 1, and (**b**) 5 wt.% of Cu for Di ethylene Glycol/ZrO_2 system.

conduction of the samples. As the temperature is increased, the ZrO_2 can exchange lattice oxygen with surface and the gas. The dramatic effect of Zirconium on LPG selectivity needs further investigation.

3. CONCLUSION

The DEG embedded ZrO_2-based materials used in gas sensors have received great attention. The high and selective absorption properties of DEG embedded ZrO_2 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 application of composite materials partially composed of a DEG, opens novel ways for choosing gas sensor materials as well. However, much more work remains to be done. Overall, we foresee that DEG embedded ZrO2 will become widely available material for gas sensing in the next few years.

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