Diethylene Glycol Embedded ZrO_2 as a Gas Sensor

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Abstract

In this paper, the preparation of polymer Di ethylene Glycol (DEG) embedded ZrO2 films at ~ 100ºC by using spray pyrolysis technique and their LPG sensing characteristics at 1000 ppm are reported. The films are prepared at different wt. % concentrations of DEG. The LPG sensing responses of these films are recorded at different operating temperatures. From LPG sensing studies, the better sensitivity values 120 (at T = 45ºC) and 100 (at T = 35ºC) are found for the films obtained at 1 and 5 wt. % of DEG respectively. The gas sensing characteristics is strongly influenced by DEG concentration.

Keywords: ZrO_2, Di ethylene Glycol; Thin films; LPG gas sensor.

1. Introduction

Now days, there has been increasing of ecological perception, fitness, and safety involving greenhouse gasses, inflammable and poisonous gases etc. As a result, there is an emergent requirement of reliable and contemptible gas sensor [1-5]. Polymer embedded Metal oxide semiconductor is the most widely used to detect oxidizing gases and prevent it from wetness atmosphere. Moreover, there are well new ways to improve Metal Oxide semiconductor sensor by modifying the surface morphology with the help of polymer embedded technique [6, 7].

In the present study, we are describing the synthesis of Polymer embedded Metal oxide film using the spray technique with an organic structure-directing agent in synthesis process. The samples obtained from polymer embedded metal oxide films were heated up-to a particular temperature. Finally, the samples after heat treatment were characterized as a gas sensor-using surface measurement system. The film sensor consisted of electrode pads. The sensor performance is investigated on gas flow at various temperatures.

2. Experimentation

Standard commercially available zirconium oxychloride (99.8 % pure, Sisco Research Pvt. Ltd.) and pure Diethylene Glycol (S.D. Fine Chime Ltd.) were used to prepare the diethylene glycol embedded ZrO_2 films. To prepare films, initially, separate 1 molar solutions of diethylene glycol and zirconium oxychloride were prepared in double distilled water. Five different solution mixtures were prepared by mixing the solutions of diethylene glycol and zirconium oxychloride in the volume ratio of 1:99, 2:98, 3:97, 4:96, and 5:95. Thin film of each of mixture solution was prepared by using spray pyrolysis method on thoroughly cleaned glass slide substrate. The LPG gas sensing properties were studied for all the films by recording the change in the voltage across the sample by half bridge method. Since the resistance of film was very high, the voltage drop across it was very large. The values of resistances of the film at different temperatures were calculated when exposed to ambient air (R_a) and LPG (R_g) gas. The sensitivity factor (SF) was calculated by using relation, SF = $(R_g/R_a)*100$.

3. Results and Discussion

3.1. Sensor study

As already reported, the gas sensitivity is 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 ($|R|_{air}$). The sensor study is optimized for following condition (i) temperature selectivity (ii) optimization of weight concentration.

3.2. Temperature selectivity

Fig. 1 shows the Variation of SF (sensitivity factor) with optimum operating temperature for LPG gas (1000 ppm) for 1, 2, 3, 4, and 5 wt. % of Di ethylene Glycol embedded ZrO_2. It can be seen that for 1 wt. % film sample, the sensitivity up to 37 °C is almost constant and then increases rapidly to maximum value at 45°C and then further decreases up to 57 °C and finally again remains constant. The flat response is obtained for the samples of 2, 3, and 4 wt. % of Di ethylene Glycol at all the temperatures in range of 30 - 80 °C. However, it is found that sensitivity to 5 wt. % film sample is maximum at lower temperature of 35 °C, but the temperature window for 1 wt. % samples is less as compared 5 wt. %.

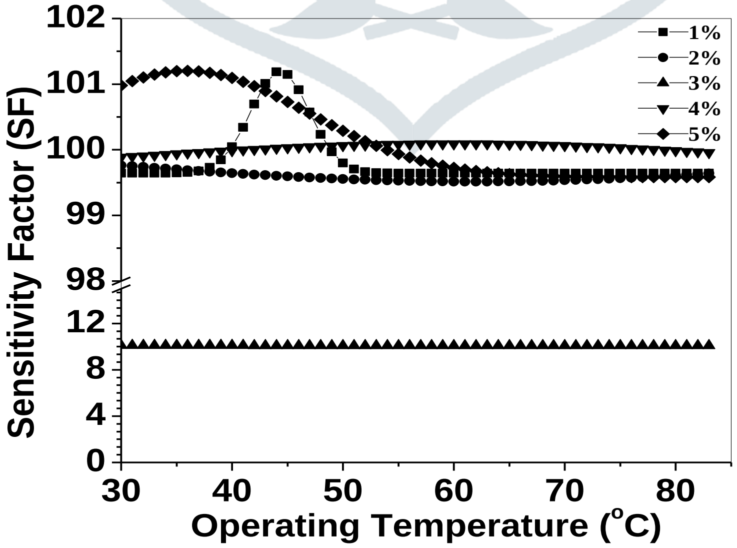

Fig. 1 Variation of SF (sensitivity factor) with temperature for LPG gas (1000 ppm) for 1, 2, 3, 4, and 5 wt. % of Di ethylene Glycol embedded ZrO_2

3.3. Optimization of weight concentration

Fig. 2 (a) reveals that 1 wt. % Di ethylene Glycol embedded ZrO_2 film sample gives more sensitivity, SF = 101. 20 at 47 °C as compared to 2, 3, 4 wt. % Di ethylene Glycol embedded ZrO_2 film samples.

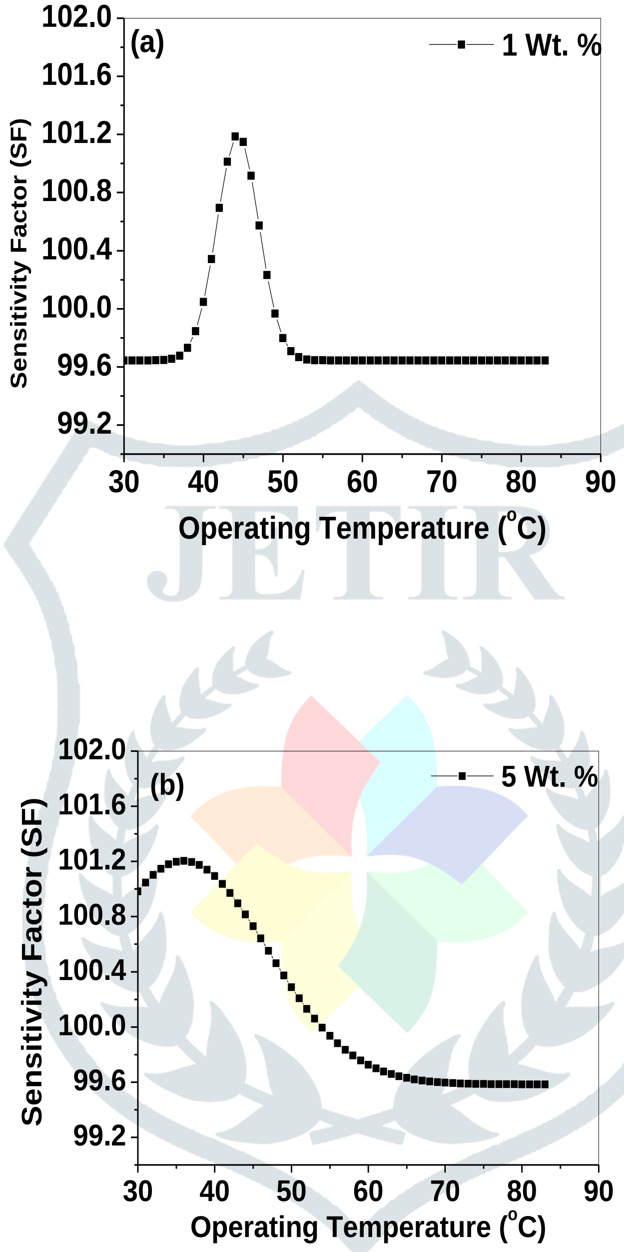

Fig. 2 Variation of SF with temperature for LPG gas (1000 ppm) for (a) 1 and (b) 5 wt. % of Di ethylene Glycol embedded ZrO_2

The 5 wt. % Di ethylene Glycol embedded ZrO_2 film sample [fig. 2 (b)] gives less sensitivity, SF= 101.18 at lower operating temperature of 37°C. It seems that both adsorption and combustion of the reducing gases occur 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 [8 - 10]. 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. 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:

$$O_2\text{ (air)} + 4\,e^- \text{ (conduction band)} \rightarrow 2O^{2-} \text{ (film surface)} \qquad -(1)$$

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 and liberate free electrons in the conduction bands. The reaction that takes place is as:

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

This shows the n-type conduction mechanism. Thus generated electron contributes to sudden increase in 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 ZrO_2 on LPG selectivity needs further investigation.

4. Conclusions

The polymer embedded ZrO_2-based materials have received great attention in gas sensing application. The high and selective absorption properties of polymer embedded ZrO_2 towards a specific gas greatly enhance the sensing selectivity for the gas. The compound or cluster sensing towards a gas assembled into the cages or channels of polymer embedded ZrO_2 results in its high stability, and maximally elevate the sensing property of the materials. The better LPG gas sensing properties of Di ethylene Glycol embedded ZrO_2 shown in the present work supports the above mentioned gas sensing characteristics of polymer embedded ZrO_2-based materials.

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