Effect of Initialization Time on Application Potentiality of a ZnO Thin Film Based LPG Sensor

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A prototype electronic LPG (Liquid Petroleum Gas) sensor based on zinc oxide (ZnO) film has been fabricated. The objective of the present work was to investigate the importance of initialization time (also called warm-up time) on the application potentiality of the ZnO based alarm. The role of sensor geometry on initialization time is presented. The electronic circuitry of the prototype LPG device alarm is discussed. It is shown that the initialization time depends on the switch off time (or the time for which the sensor was kept idle). The resistive mode sensors can be fixed at 40% LEL (Lower Explosive Limit) of LPG for safe operation.

Keywords: ZnO thin film, lpg sensor, initialization time, prototype alarm

1. Introduction

It is long known that resistance of oxide semiconductors decreases in presence of a reducing gas. Accordingly the phenomena of gas sensitivity have been a subject of wide research and resistive mode gas sensors based on SnO₂ is the most commercially exploited. The characterization of gas sensors normally involves study of a few parameters e.g., sensitivity, response time, stability, selectivity, recovery time, stability and selectivity. On exposure to a reducing target gas, the sensor resistance decreases quite rapidly and thereafter reaches a stable value. This value of sensor resistance is called the equilibrium resistance value of the sensor in presence of target gas. From this value of equilibrium resistance ($R_{g,eq}$), percent sensitivity of ($S\%$) the sensor can be evaluated from the relation

$$S\% = \left[1 - \frac{(R_g)_{eq}}{R_a} \right] \times 100 \quad (1)$$

where R_a is the sensor resistance in air prior to the exposure of target gas.

The response time (τ_r) is normally defined as the time required to reach 90% of the difference [$R_a - (R_g)_{eq}$] after sudden change of the atmosphere from a state with no gas (i. e. air) to that containing the target gas¹⁻². The recovery time similarly is defined as the time it takes to reach 90% of the difference [$R_a - (R_g)_{eq}$] after the reverse change of atmosphere¹.

Apart from the above parameters, initialization time or warm-up time is a very important parameter, which determines the application potentiality of the sensors. The sensors are used in the resistive mode and at temperatures higher than room temperature. Thus, when it is heated from room temperature to the working temperature, it requires some time to attain the operating temperature and initial equilibrium resistance in air. In other words, initialization time (τ_i) is the time required by the sensor element to attain the initial resistance in air (i.e. time for attaining R_a) from switch off (idle) condition. Once it attains R_a , the sensor is ready to operate. The warm up time in turn depends on the geometry of the sensor assembly apart from intrinsic material property. The effect of warm up time on the application prospect of a ZnO based sensor material is discussed in the present work. The importance of miniaturization of sensor assembly in this

regard is presented. A suitable electronic circuitry for the sensor materials has been designed.

2. Experimental

2.1. Fabrication of the sensor element

The fabrication of the sensor element on a cylindrical glass tube of 5 mm length, 2 mm external diameter and 1 mm internal diameter has been reported earlier³⁻⁴. In brief, the process involves multiple dipping of the substrate (glass tube) in sodium zincate (Na_2ZnO_2) bath (0.1 M) maintained at room temperature and hot water bath maintained near boiling point. The zincate complex was prepared by adding sodium hydroxide ($NaOH$) in a solution of zinc sulphate ($ZnSO_4$). The reaction leading to the formation of ZnO on the substrate is as follows: $Na_2ZnO_2 + H_2O = ZnO + 2NaOH$.

Dipping of the substrate in zincate bath results in a thin layer of the zincate solution on the substrate. Subsequent dipping of the substrate in hot water leads to breaking down of the complex and formation of ZnO. The film thickness was built up by increasing the number of dipping. The growth rate is $\sim 0.025 \mu\text{m}$ per dipping and 100 dipping gives a film of $\sim 2.5 \mu\text{m}$. The surface of ZnO film was sensitized with palladium (Pd) by dipping the film in a 50 cc solution of 1 wt. (%) solution of palladium chloride ($PdCl_2$) in ethyl alcohol (C_2H_5OH)^[3-4]. 15-20 dipping was found to be optimum to get sensor with stable film resistance³. Enhanced number of dipping results in a continuous conducting film making the sensor ineffective for operation. The Pd treated film was subsequently annealed in air at 250 °C for 1 hour.

A nichrome wire (80 gauge), used in the form of a heating coil was placed inside the hollow tube, in order to operate the sensor element at the requisite working temperature. Electrical contacts with silver (Ag) paste on the film were made at the two ends of the cylindrical sensor element. The solder connections on a standard 6-pin base and the housing of the sensor element on a polycarbonate base with a polycarbonate cover (12 mm inner diameter and 8 mm height) were reported earlier. Stainless steel (SS) wire gauge (100 mesh) was fixed

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Figure 1. As-deposited and Pd-treated sensor element on glass tube and sensor assembly housed inside a polycarbonate casing.

Figure 2. Electronic Circuit of LPG alarm (Schematic arrangement of the alarm circuit used for the Pd-sensitized ZnO sensor).

on the polycarbonate frame through which the target gas could come in contact with the sensor element. Figure 1 shows as deposited and Pd treated sensor elements as well as few typical complete sensor assemblies.

2.2. Electronic circuit of the prototype electronic alarm

Figure 2 shows a prototype electronic alarm based on the sensor assembly. The property of decreasing resistance in presence of LPG is utilized to initiate a triggering circuit to generate an alarm. The circuit operates at 5 V DC power supply. When the power is switched on, the sensor reaches the operating temperature after the initial action i.e. warm-up time. A standard resistor $R_0 \cong 20 \text{ k}\Omega$ (also called dropping resistor⁵) is connected in series with the sensor element. On exposure to target gas (LPG for the present case), the sensor resistance and hence the voltage across the sensor decreases sharply. When the sensor voltage dropped below a certain preset value (alarm setting) the comparator output activates a warning buzzer. When LPG is removed from the sensor environment, the sensor resistance and

Figure 3. Warm-up time, sensing and recovery characteristics of the sensor element.

the corresponding voltage across it increased and the warning buzzer turns off when the sensor voltage went above the alarm setting.

3. Results and Discussions

3.1. Warm-up time, sensing and recovery characteristics

Figure 3 shows the warm-up time, the sensing and recovery characteristics of the ZnO based sensor element in presence of 1.6 vol. % LPG in air [which corresponds to 80% LEL (Lower Explosive Limit) of LPG in air] at 250 °C. The target gas concentration was fixed by adjusting the flow rates of the target gas and air (carrier gas) through a pre-calibrated Mathiesson flow meter. From the study of temperature dependence of sensitivity, the choice of optimum temperature was made around 250 °C³. The sensing and recovery characteristics for four measurements are shown in the Figure 3 in terms of actual sensor resistance for convenience.

The heater power required to operate the sensor at the optimum temperature of 250 °C is about 1.0 W. The figure shows that immediately after the power is switched on, the sensor resistance decreases and then gets stabilized. The initial sharp fall of resistance is due to semiconducting nature of the ZnO thin film. This is followed by an increase in resistance before being stabilized at around 2 M Ω . This is the initial value of the equilibrium sensor resistance in air (R_a). The stabilization of the sensor resistance results from the equilibration of the chemisorption process. The most stable species at 250 °C is the O^- species^{3,6} and the stabilization was achieved when an equilibrium concentration of these adsorbed species was obtained.

As has been mentioned earlier, the time required to reach the operating condition is called the warm-up time of a sensor material. The target gas is then allowed to fall on the sensor element. The average sensitivity of $88.2 \pm 2.7\%$, average response time of 23.02 ± 3.0 seconds and average recovery time (corresponding to complete or 100% recovery) of 60.0 ± 8.0 seconds was also reported. The time for 80% recovery was however, less than 30 seconds and beyond this time, the sensor can be considered to be ready for the next sensing cycle.

Sensors prepared under similar conditions gives more or less identical sensor parameters (in terms of sensitivity, response and recovery times) within the limits of experimental error. Experiments were carried out for three sensor elements and data for one representative element is

Figure 4. Attainment of operating temperature (250 °C) in two different sensor assemblies: (O) 1 mm I. D. 5 mm tube, nichrome heating coil, (Δ) 3.3 mm I. D. 15 mm length tube, kanthal heating coil.

presented. Sensitivity was found to be within 85-92% for all the sensor elements. The average response time was between 19-27 seconds and the recovery time was between 50-70 seconds.

3.2. Effect of miniaturization of sensor assembly

It is seen from Figure 3 that the warm-up time is around 3 minutes after which the sensor can be said to be ready to operate. In this connection it is to be mentioned that temperature measurement was carried out on the surface of the cylindrical tube (substrate) by using a platinum (Pt) wire. A direct current (DC) source was used to supply power to the heater coil. The resistance measurement of the platinum wire having known value of temperature coefficient of resistance directly gives the temperature of the sensor. The temperature of 250 °C is reached by applying 1.0 W power.

We reported another sensor assembly⁷ for methane sensitivity of ZnO thin films where kanthal wire (30 SWG) was used as the heating element. The sensor element was mounted on a teflon base with copper (Cu) pins. The mounted sensor was covered with a small brass cover having gas inlet and outlet tubes which allowed the target gas to come in contact with the sensor element. The brass cover was of 20 mm inner diameter and 10 mm height. The sensor element was fabricated on glass or alumina substrate of 15 mm length, 3.3 mm internal diameter, 6.5 mm external diameter and wall thickness was about 1.6 mm. A temperature of 250 °C required approximately 7 W in this assembly. It is clearly evident that the requisite temperature of 250 °C is obtained at a much lower wattage (1.0 W with the present design compared to 7.0 W with the earlier design) with the miniaturized sensor assembly.

Moreover, the time required to reach the operating temperature is much lower due to low thermal mass of the sensor assembly as evident from Figure 4. The low thermal mass results from miniaturization of the sensor assembly. Thus miniaturization of the sensor assembly is extremely important for device point of view since the warm-up time is reduced. The low thermal mass ensures low wattage and less heating time.

It appears that still further lowering of initialization time is possible for microsensors with microheaters fabricated by MEMS. Miniaturization of sensor assembly helps to attain the operating temperature at a shorter time. The attainment of operating temperature and equilibrium sensor resistance (which is a two stage process including the time for initial sharp fall due to semiconducting nature of ZnO and subsequent increase of resistance due to chemisorption process)

Figure 5. Variation of sensor voltage with time for different idle time of the sensor element (□) 6 hours, (O) 12 hours, (Δ) 18 hours and (▽) 24 hours.

proceeds simultaneously. Thus, faster the operating temperature is attained, shorter will be the time required for attaining the equilibrium sensor resistance in air (R_a).

3.3. Effect of initialization time on alarm setting

The electrical resistance of the sensor element can be evaluated from the voltage drop across the standard resistor. Thus if V_{dc} is the applied voltage (5 V in this case), then $V_{dc} = V_s + V_0$, where V_s and V_0 the voltage drops across the sensor and the standard resistor. This gives the value of sensor resistance as

$$R_s = \left(\frac{V_{dc}}{V_0} - 1 \right) R_0 \quad (2)$$

a value of $R_s \approx 0.22 \text{ M}\Omega$ (which corresponds to ~89% sensitivity, see figure 2) gives $V_s \approx 4.58 \text{ V}$, since the standard resistor was selected as $R_0 \approx 0.20 \text{ k}\Omega$. Thus, if the alarm is setting is made at ~4.6V, it will be able to detect 1.6 vol % LPG in air within 23 ± 3 seconds. Normally for device applications, faster response time is preferable. The alarm setting can be adjusted to a suitable preset value so that it can activate the output within a few seconds. For example, instead of setting the alarm at ~89% resistance reduction level (for which the response time is calculated to be 23 ± 3 seconds), it can be set at 80% resistance reduction level in which case the presence of the gas can be detected within ~15 seconds. Therefore the alarm level of the present detector can be fixed at 4.75V (which corresponds to 80% resistance reduction level). Alarm setting at 60-70% resistance reduction level makes the response even faster.

It is to mention in this connection that the warm-up time depends on the time for which the sensor was kept off or kept idle. Longer is the time the sensor is kept idle (i.e. switched off), more is the time required for the sensor to attain the initial equilibrium resistance in air (R_a) i.e. to reach the working condition. Figure 3 shows the sensor voltage against time immediately after the switch is on or power is applied. Figure 5 shows the initialization time when the sensor is made to operate after some idle time. For an idle time of 6 hours, the sensor requires 4 minutes to reach the to reach $R_a \approx 2 \text{ M}\Omega$. However, it requires 15, 60 and 90 minutes to reach $R_a \approx 2 \text{ M}\Omega$ for idle times of 12, 18 and 24 hours respectively. In practice, the sensor can be ready to operate when the sensor voltage crosses the alarm set value of 4.75 V. It requires 2, 10 and 30 minutes for idle times of 12, 18 and 24 hours respectively. The alarm will produce continuous signal during these times. As soon as V_s crosses 4.75 V, the sensor is ready to produce

signals in presence of target gas. The sensor resistance corresponding to this value of alarm setting is $R_s \approx 0.38 \text{ M}\Omega = 380 \text{ k}\Omega$. The sensor can be said to in dynamic equilibrium between $R_s \approx 0.38 \text{ M}\Omega$ and $R_s \approx 2 \text{ M}\Omega$ where it can detect the incoming target gas.

As has been already mentioned that stabilization of sensor resistance in air requires attainment of equilibrium concentration of O^- adsorbed species on the surface of the thin film. The process of uniform surface coverage by charged species is an exponential one and requires long time⁶. The problem doesn't appear if the sensor is kept idle for small time (less than six hours or so), since the already adsorbed species do not get sufficient time to get desorbed. The process of desorption also requires long time. Longer the sensor is kept idle, larger is the time required for attaining this surface coverage since the adsorption process starts afresh. Adsorption of water molecules also plays a role in the process. Longer the idle time of the sensor material, more water molecules get adsorbed as hydroxyl ions, which are difficult to whip off.

3.4. Selectivity and stability

Both selectivity and stability are crucial parameters for any practical applications. Not much systematic study on selectivity has been made in the present work. However, as expected, the sensors were found to be highly sensitive to hydrogen at 250 °C (~99%), the operation temperature used for LPG alarm device. On the other hand the sensitivity to methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) was found to be relatively low at this temperature. The economic consideration of large-scale production is guided by the stability of the sensor device. Although no systematic study was carried out to check the stability of the sensor materials, it was found that the material exhibits stable continuous operation for sixty days at a stretch without any significant degradation. The instrument was kept on continuously for a period and periodically tested in low concentrations of LPG ambient. There was negligible zero drift for the continuous operation for 60 days and sensor functions were stable during this period. However, around 5% decrease in sensor resistance at operating temperature of 250 °C was observed after 60 days continuous operation. The sensitivity and response time was also found to be slightly affected after this period of operation. After ninety days of continuous operation (idle time not exceeding 6 hours was provided at irregular intervals), there was degradation in sensor functions almost making it unusable. Accordingly, the maximum self-life of the present sensors is only 3 months.

4. Conclusions

The result of the present investigation suggests that the ZnO based sensor element sensor cannot be kept idle for more than 12 hours since it requires abnormally high time to get ready for operation. Thus even when it is not in use, it is to keep powered. Lowering down the alarm setting can decrease the initialization time, but this increases the response time to target gas. The problem of large initialization time and high response time can be resolved by increasing the sensitivity. In this case the alarm setting can be made lower and adjusting the alarm set at a suitable value can make response time faster. This can be possibly achieved using other catalysts like platinum (Pt), silver (Ag) or gold (Au). Experiments in this direction are in progress.

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