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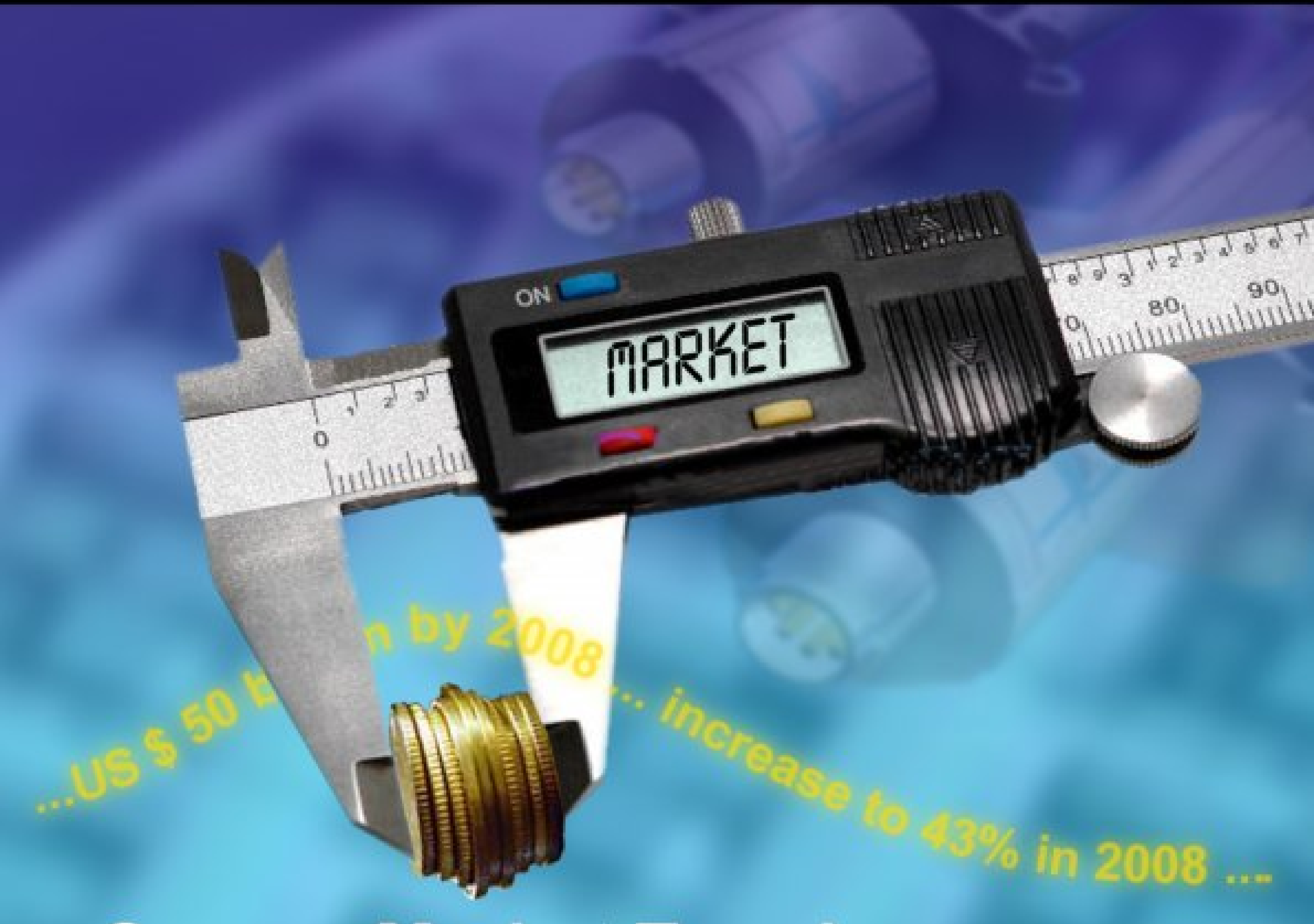

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Surface Activated ZnO Thick Film Resistors for LPG Gas Sensing

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Abstract: The CuO-modified films obtained by dipping pure ZnO thick films into an aqueous solution of copper chloride for different intervals of time and fired at 500^0C for 24 h. The copper chloride would transform into copper oxide upon firing. CuO-modified (0.4092 mass % CuO) ZnO thick films resulted in LPG gas detector. Upon exposure to 1000 ppm LPG gas, the barrier height between CuO-ZnO grains decreases markedly leading to a drastic decrease in resistance. An exceptional sensitivity was found to LPG gas at 400^0C and no cross sensitivity was observed to other hazardous and polluting gases. The instant response (~ 5 sec) and fast recovery (~ 10 sec) are the main features of this sensor. The effects of microstructure and surfactant concentration on the gas response, selectivity, response time and recovery time of the sensor in the presence of LPG gas were studied and discussed.

Keywords: Zinc oxide, CuO-modified ZnO, LPG gas sensor, gas response and recovery time.

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1. Introduction

Liquefied Petroleum Gas (LPG) is highly inflammable gas. It is explosively utilized in industrial and domestic fields as fuel. It is referred as town or cooking gas. Cooking gas consists chiefly of butane (55-vol %) [1], a colorless and odorless gas. It is usually mixed with compounds of sulfur (methyl mercaptan and ethyl mercaptan) having foul smell, so that its leakage can be noticed easily. This gas is potentially hazardous because explosion accidents might be caused when it leak out by mistake. It has been reported that, at the concentration up to noticeable leakage, it is very much more than the lower explosive limit LEL of the gas in air. So there is a great demand and emerged challenges [2] for monitoring it for the purpose of control and safety applications in domestic and industrial fields. ZnO crystallizes in a wurtzite structure showing n-type semiconductivity [3, 4]. ZnO utilized in wide range of applications [5-11].

The aim of the present work is to develop the sensor by modifying ZnO thick films, which could be able to detect the LPG gas. Among the various metal oxide additives tested, CuO in ZnO is outstanding in promoting the sensing properties to LPG in air.

2 Experimental

2.1 Thick film preparation

AR grade (99.9 % pure) zinc oxide powder was ball milled to ensure sufficiently fine particle size. The fine powder was calcined at 1100^0C for 24 h, in air and re-ground. Thick films of, so obtained powder, were prepared by adopting the procedure explained elsewhere [12, 13].

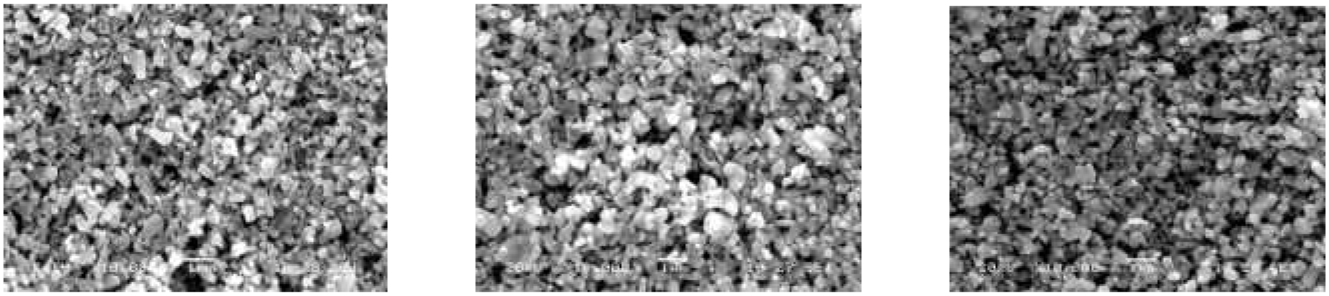
2.2 Characterization

The microstructure and chemical composition of the films were analyzed using a scanning electron microscope (JOEL JED 2300) coupled with an energy dispersive spectrometer (6360 LA). Thickness measurements were carried out using a Taylor-Hobson (Talystep, UK) system. Electrical and gas sensing characteristics were measured using a static gas sensing system.

3. Materials Characterization

3.1 Microstructure -SEM

Figs.1 (a-c) depict the microstructure of unmodified ZnO, CuO-modified ZnO for 5 min and 30 min respectively. Fig. 1(a) consists of randomly distributed grains with larger size and shape distribution. Fig.1 (b) consists of CuO grains with smaller size and shape associated with the ZnO grains. CuO grains may reside in the intergranular regions of ZnO. Thus effective surface area was expected to be increased explosively. Fig.1 (c) consists of large number of smaller particles of Cu-species distributed on the surface of the ZnO film. Few Cu-species are percolated in the bulk, results in decreasing the mass % of Cu-species on the surface of the film.



(a) (b) (c)

Fig.1. SEM of (a) Unmodified ZnO, (b) Modified ZnO (5 min) and (c) Modified ZnO (r 30 min).

3.2 Thickness and Thermoelectric power measurements

The thicknesses of the films were observed to be in the range from 20 to 25 µm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste. The p- or n-type semi-conductivity of thick films of CuO and ZnO were confirmed by measuring thermo electromotive force of the thick film samples. The ZnO was observed to be n-type and CuO the p-type material.

3.3 Elemental analysis

Pure white ZnO is expected to be stoichiometric and showing insulating properties. The pure white ZnO powder turns yellow on calcination at higher temperature (~ 1100^0C for 24 h). It is because of deficiency of oxygen [3, 4]. Stoichiometric mass % of Zn and O in ZnO are 80.34 and 19.66 respectively. The mass % of Zn and O in each sample was not as per the stoichiometric proportion and all samples were observed to be the oxygen deficient (Table 1). This leads the non-stoichiometricity in the solid and formation of n-type semiconductor.

Table 1. Quantitative Elemental Analysis of unmodified (pure) and CuO-modified films.

Elemental Mass %	**Dipping Time (min.)**				
	0	2	5	15	30
Cu	0.00	0.07	0.33	0.41	0.33
O	8.06	8.77	11.30	8.11	11.18
Zn	91.95	91.16	88.38	91.48	88.49
ZnO	100	99.91	99.59	99.49	99.58
CuO	0.00	0.09	0.41	0.51	0.42
CuO-ZnO	100	100	100	100	100

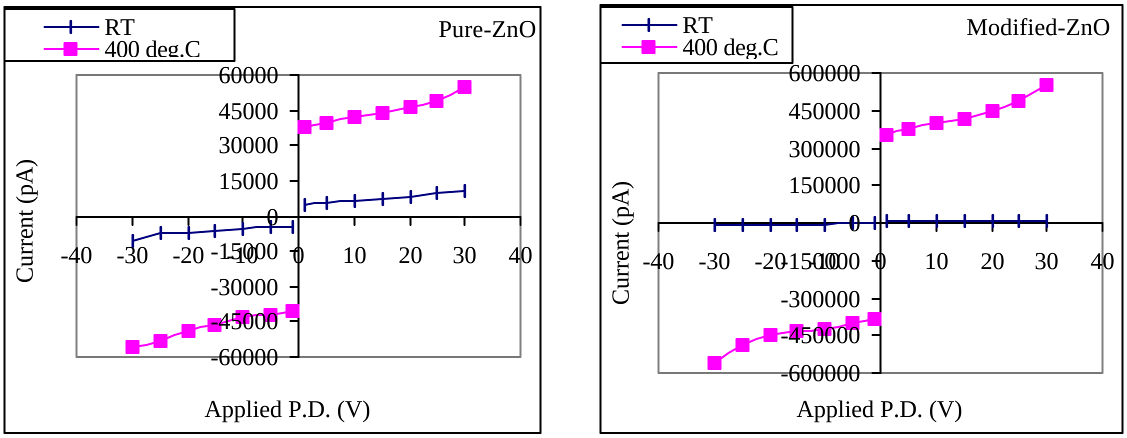
4. Electrical Properties

4.1 I-V Characteristics

I-V characteristics of pure and modified ZnO are observed to be symmetrical in nature indicating ohmic nature of silver contacts. Figs.2 (a, b) depict the conductivities of pure and modified ZnO at room temperature and at 400^0C.

4.2 Electrical resistivity

The semiconducting nature of ZnO is observed from the measurements of resistivity with temperature. The semiconductivity in ZnO must be due to large oxygen deficiency in it. The material would then adsorb the oxygen species at higher temperatures ($O_2^- \rightarrow 2O^- \rightarrow O^{2-}$). The adsorption chemistry of CuO-modified ZnO surface would be different from the pure ZnO thick film surface. The CuO misfits on the surface are the places where the oxygen species adsorbs.



(a) (b)

Fig.2. I-V characteristics of the sensor.

The CuO misfits distributed evenly on the surface would have made it possible to adsorb the oxygen ions even at low temperatures. From Fig.3 it is clear that, the resistivity of CuO-modified film decreases with increase in operating temperature indicating negative temperature coefficient of resistance. This behavior confirmed the semiconducting nature of modified ZnO. The drastic increase in the conductivity of CuO-modified ZnO at 400^0C than at room temperature (Fig.2 (b)) could be attributed to the charge-carrier generation mechanism resulted from the electronic defects can be described in the Kroger-Vink [14, 15] notation as:

$$3CuO_{ZnO} \xrightarrow{400\ (deg.C)} 3Cu^{2+}_{Zn} + 2\,O_O + \frac{1}{2}O_2\uparrow + 6e^-$$

These generated electrons and the donor level in the energy band gap of ZnO will contribute to increase in conductivity.

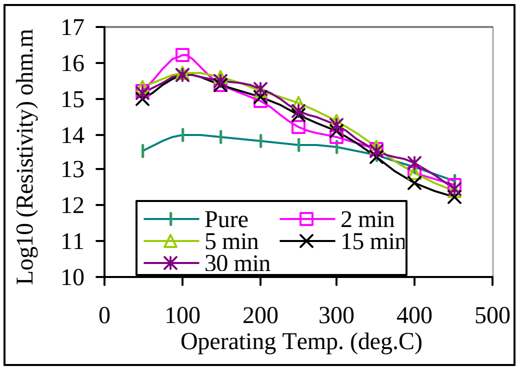


Fig.3: Variation of log (resistivity) with operating temperature.

5. Sensing Performance

5.1 Measurement of Gas response, Selectivity, Response and Recovery time

Gas response *(S)* is defined, as the ratio of change in conductance of the sensor on exposure of the target gas to the original conductance in air medium. The relation for s is as:

$$S = (G_g - G_a) / G_a$$

where, G_a is the conductance of sensor in air medium and *7* is the conductance of sensor in gaseous medium.

Selectivity or specificity is defined, as the ability of a sensor to respond to certain gas in the presence of more gases. Percentage selectivity factor of one gas over other is defined as, the ratio of the maximum response of other gas to the maximum response of the target gas at optimum temperature.

$$\% \text{ Selectivity factor} = (S_{gas} / S_{target\ gas}) \times 100 \ \%$$

The time taken for the sensor to attain 90 % of the maximum change in conductance on exposure to the target gas is the response time. The time taken by the sensor to get back 90 % of the original conductance is the recovery time.

5.2 Sensing performance of pure ZnO thick film

Fig. 4 depicts the variation of gas response with operating temperature of pure ZnO thick film for 1000 ppm LPG gas. In case of pure ZnO, oxygen adsorption seems to be poor which may the result of poor response. In addition to this, ZnO requires relatively larger operating temperature to adsorb the oxygen ions, and therefore it would have responded at higher operating temperature. To improve the sensing performance of ZnO, it is essential to modify its surface.

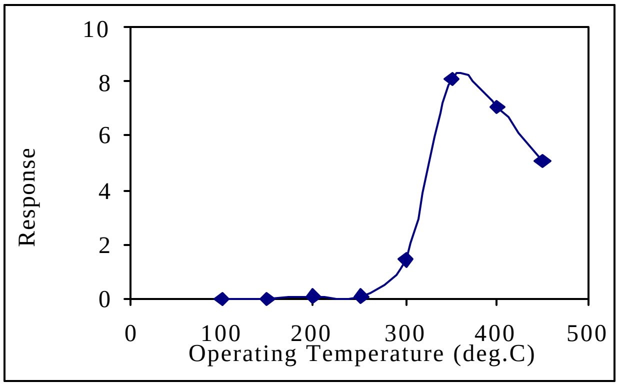


Fig. 4. Variation of response with operating temperature.

5.3 Sensing performance of CuO-modified ZnO Thick Film

5.3.1 Response and gas concentration

For CuO-modified ZnO film, the response was observed to increase continuously with increasing the gas concentration up to 1000 ppm at 400^0C (Fig.5). The active region of the sensor would be between 100 to 1000 ppm; as the rate of rise of response is larger during this region. At lower gas concentrations, the unimolecular layer of gas molecules would be expected to be formed on the surface, which would interact with the surface more actively giving larger responses. There would be multilayers of gas molecules on the sensor surface at the higher gas concentrations resulting in saturation in response.

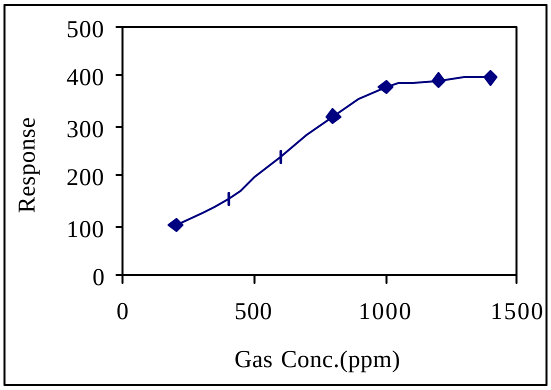
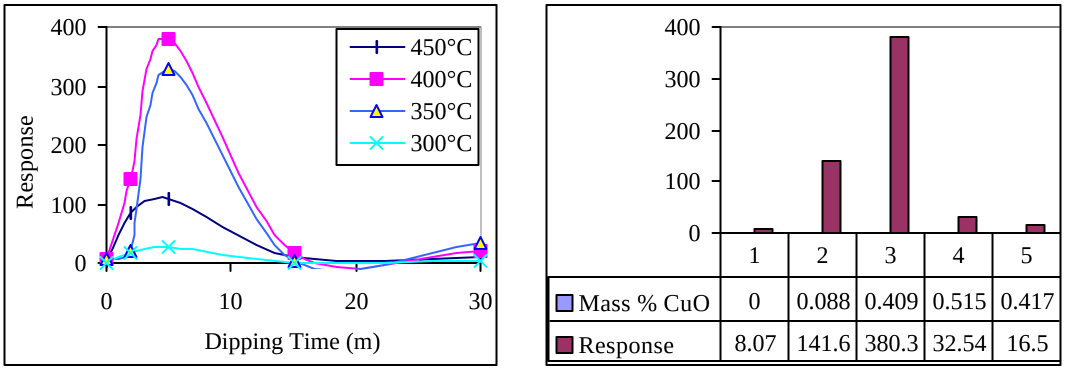


Fig.5. Variation of gas response with gas concentration.

5.3.2 Gas response, dipping time and Cu-surfactant

Fig. 6 (a, b) depict the variation of gas response with dipping time and Cu-surfactant. The film dipped for 5 min. showed highest gas response (380.25). At 5 min. dipping time, the optimum mass % of CuO (0.4092) would dispersed on the surface of the film, and mass % of oxygen was also high (11.2984) (Table 1). The highest gas response of CuO-modified ZnO would be explained as follows. The optimum mass % of CuO on the surface of ZnO would form misfit regions uniformly on the film surface. The adsorption mechanism of CuO modified ZnO would be different from pure ZnO. The number of oxygen ions adsorbed on the modified surface would be larger. Larger the number of oxygen ions adsorbed, faster and quicker would be oxidization of LPG gas. This would increase the conductance of the film drastically, enhancing gas response. It is observed from Fig.6 (b) that, the gas response is largest at 0.4092 mass % of the cu-surfactant on the surface of the film. At higher mass %, the Cu-surfactant would mask the base material-ZnO and would resist the gas to reach up to the surface sites and gas response would decrease.



(a)

(b)

Fig. 6. Variation of gas response with (a) dipping time and (b) Cu-surfactant.

5.3.3 Gas response and operating temperature

It is clear from figure 7 that, the gas response increases with operating temperature; reaches to maximum (380.25) at 400^0C, and falls with further increase in operating temperature. The LPG may burn before reaching the surface of the film at higher temperature (> 400^0C). Hence, gas response may decrease above 400^0C. At 400^0C, larger amount of oxygen would be adsorbed on the surface, which would facilitate the sensor to oxidize the target gas (LPG) immediately giving faster and larger gas response.

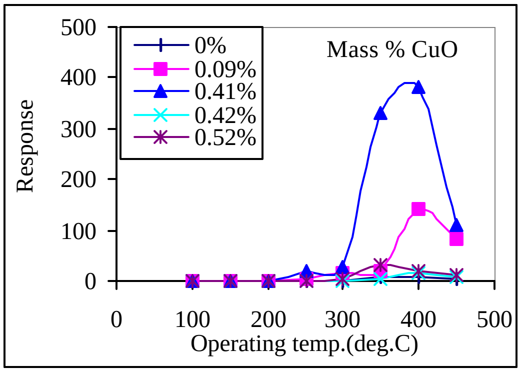
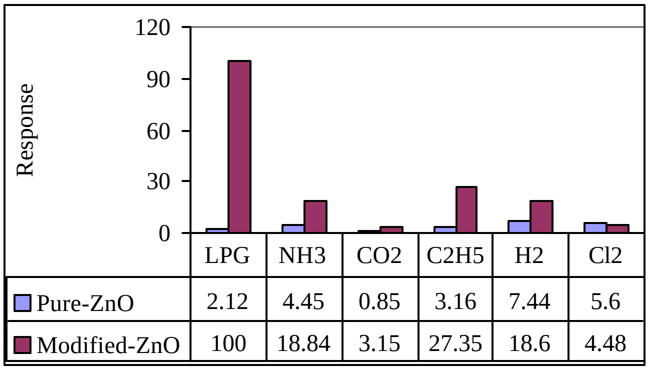


Fig. 7. Variation of gas response with operating temperature.

5.3.4 Selectivity for LPG against various gases

Fig.8 depicts the % selectivity factor of the CuO-modified ZnO (calcined at 1100^0C for 24 h with 0.4092 mass % of CuO) to 1000 ppm of LPG gas against various gases at 400^0C. It is clear from Fig.8 that in contrast to pure zinc oxide the sample showed not only enhanced response towards LPG but also very high selectivity.



	LPG	NH3	CO2	C2H5	H2	Cl2
🟦 Pure-ZnO	2.12	4.45	0.85	3.16	7.44	5.6
🟪 Modified-ZnO	100	18.84	3.15	27.35	18.6	4.48

Fig.8. Gas response among various gases.

6. Discussion

Table 2. Composition of LPG gas.

Composition (Vol %)	CH_4	C_2H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}
	6	8	11.5	15	55	4.5

As the butane is the major constituent of LPG (Table 2), it requires high temperature to dissociate into lower alkanes. Carbon-carbon and carbon-hydrogen bonds are quite strong due to strong Vander Waals forces. They break only at higher temperatures resulting in carbon and hydrogen separation. The atmospheric oxygen O_2 adsorbs on the surface of the thick film. It captures the electrons from conduction band as:

$$O_{2\,(air)} + 4e^- \rightarrow 2O^{2-}_{(film\ surface)}$$

It would result in decreasing conductivity of the film. When alkanes react with oxygen, a complex series of reactions [16-18] take place, ultimately converting the alkanes to carbon dioxide and water as:

$$CH_{4\,(gas)} + 4\,O^{2-}_{(film\ surface)} \rightarrow CO_{2\,(gas)} + 2\,H_2O_{(gas)} + 8\,e^-_{(cond.band)}$$
$$C_2H_{6\,(gas)} + 7\,O^{2-}_{(film\ surface)} \rightarrow 2\,CO_{2\,(gas)} + 3\,H_2O_{(gas)} + 14\,e^-_{(cond.band)}$$
$$C_3H_{8\,(gas)} + 10\,O^{2-}_{(film\ surface)} \rightarrow 3\,CO_{2\,(gas)} + 4\,H_2O_{(gas)} + 20\,e^-_{(cond.band)}$$
$$C_4H_{10\,(gas)} + 13\,O^{2-}_{(film\ surface)} \rightarrow 4\,CO_{2\,(gas)} + 5\,H_2O_{(gas)} + 26\,e^-_{(cond.band)}$$

This shows n-type conduction mechanism. At higher temperature, molecular oxygen O_2 becomes O_2^- and alkanes decompose producing hydrogen ions H^+ in the reaction. The anion super-oxide O_2^- reacts with H^+ giving water molecule and molecular oxygen O_2:

$$2O_2^- + 2\,H^+ \rightarrow H_2O_2 + O_2$$

Catalase

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

LPG gas on exposure decomposes into carbon and hydrogen species, which react with adsorbed oxygen, liberating the captured electrons into conduction band resulting in enhancing the catalytic activity of the film surface.

7. Summary

From the results, following statements can be made for the sensing performance of CuO-modified sensors.

1) Pure zinc oxide was almost insensitive to LPG and LNG gases.
2) Among various additives tested CuO in ZnO is outstanding in promoting the LPG gas sensing.
3) Surface modification by dipping process is one of the most suitable methods of modifying the surface of thick films.
4) 0.4092 mass % of CuO incorporated in pure ZnO thick film is the most sensitive element to LPG gas.
5) CuO-modified ZnO has the potential of fabricating the LPG sensor.
6) The sensor showed very rapid response and recovery to LPG gas.
7) The sensor has good selectivity to LPG against NH3, CO2, Cl2, H2 and C2H5OH.

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