20. Study of Cuo- ZnO Screen Printed Thick Films as LPG Sensor at Room Temperature

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Abstract

Using a screen printing technique, thick films of pure ZnOand CuO-doped ZnO wereprepared on glass substrates with various concentrations of CuOviz 1 wt. %, 3 wt. %, 5 wt. %, and 7 wt. %. The filmsamples were fired at 450°C temperature for twohours in the air atmosphere. The films were taken under the Scanning Electron Microscopy (SEM),X-ray diffraction and Energy Dispersive Spectroscopy (EDS) for the study of morphological, structural and compositional properties.Under the normal temperature conditions, the LPG gas sensing study of each sample was carried in a static gas sensing system.It was seen that surface resistance of thick films went on decreasing when exposed to LPG gas. The CuO doped films showed significant sensitivitytoLPG gas than pure ZnOfilm. 5 wt. % CuO-doped ZnO film was found to be more sensitive (88.88%) to LPG gaswhen exposed at room temperature (50^0C) than other doping concentrations with fast response and recovery time.

Keywords: ZnO; CuO; LPG; XRD; SEM;

1. Introduction

From all the gas sensing solid state materials, metal oxides were one of the first considered [1, 2] and are still the most widely used gas sensing materials. Gas sensors based on metal-oxides are commonly used in the monitoring of toxic pollutants, highly inflammable gas and can provide the necessary sensitivity, selectivity required by such systems [3]. Commonly used oxides include, zinc oxide, titanium dioxide, iron oxide, tungsten oxide and tin oxide. These materials have successfully been employed to detect a range of gas particularly ethanol, NO2,

H2S, NH3, LPG, CO2 [4–12].Thick film technology is often used to fabricate such sensors and possesses many advantages, for example, low cost, simple construction, small size and good sensing properties [13].In addition, this approach provides reproducible films consisting of a well-defined microstructure with grains and grain boundaries that can be studied easily [14]. Zinc oxide (ZnO) is a multifunctional material. Because of its high chemical stability, low dielectric constant, large electrochemical coupling coefficient and high luminous transmittance, ZnO based materials have been widely used as dielectric ceramic, pigment, catalyst and sensing material [6, 7, 8]. As a gas sensing material, it is one of the earliest discovered and most widely used gases sensing material for the detection of hazardous gases [15-19].

It is sensitive to many sorts of gases and has satisfactory stability. The gas sensing performance of the material can be improved by incorporating dopants and additives [20-24] that can modulate the gas sensing characteristics to some extent. 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 %) [25], 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 [26] 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. ZnO utilized in wide range of applications .The CuO/ZnO system is of great importance because of its use as the methanol synthesis catalyst in low-temperature water–gas shift reactions and for hydrogen production from methanol in the reverse water–gas shift reaction. No matter what the original motivation, the outcome allows us to demonstrate the usefulness of these kinds of model system studies not only for applications in heterogeneous catalysis but also for gas sensing applications [27].The aim of the present work is to study the sensor by doping ZnO thick films, which could be able to detect the LPG gas. Among the various additives tested, CuO in ZnO is outstanding in promoting the sensing properties to LPG in air.

2. Experimental Work

The ZnO: CuO pastes used in screen printing were prepared by maintaining the inorganic to organic materials ratio of 70:30. Inorganic part consists of a functional material (ZnO), dopant (CuO) .Organic parts consist of 8% ethyl cellulose (EC) and 92% butyl carbitol acetate (BCA). The Analar (AR) grade ZnO with x wt. % CuO (x = 1, 3, 5, and 7 %) were mixed thoroughly in an acetone medium with mortar and pestle. A solution of EC and BCA in the ratio 8:92 was made, which was added drop by drop until proper thixotropic properties of the paste were achieved. ZnO thick films were prepared on glass substrates using a standard screen-printing technique. A nylon screen (40s, mesh no.355) was used for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen using a standard photolithography process. The paste was printed on clean glass substrates (5 x 2 cm) with the help of a mask. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under infrared radiation for 45 minutes to remove the organic vehicle and then fired at a temperature of 450°C for 2 h (which includes the time required to achieve the peak firing temperature , constant firing for 30 minutes at the peak temperature and then to attain the room temperature) in a muffle furnace. The structural properties of ZnO: CuO films were investigated using X-ray diffraction analysis from 20-80^0 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) with CuKα, λ=0.1542 nm radiation] with a 0.1°/step (2θ) at the rate of 2 s/step. A scanning electron microscopy (SEM-JOEL JED-2300) was employed to characterize the surface morphology. The composition of ZnO: CuO thick film samples were analyzed by an energy dispersive X- ray spectrometer (JOEL-JED 6360 LA). The thickness of the films was measured using a Taylor-Hobson (Taly-step UK) system and was observed to be uniform in the range of 20μm to 25μm.

The specific surface area was calculated for spherical particles using the following equation [28].

$$Sw = 6/\rho d \quad \text{---------- (1)}$$

where d is the diameter of the particles, ρ is the density of the particles.

The D.C. resistance of the films was measured by using half bridge method in an air atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system Figure 1 [29] under normal laboratory conditions. The electrical resistance of thick films in air (R_a) and in the presence of LPG (R_g) was measured to evaluate the gas response (S) given by the relation,

$$S = \frac{R_a - R_g}{R_a} \text{ ---------- (2)}$$

where R_a is the resistance of the ZnO: CuO thick films in air and R_g is the resistance of the ZnO: CuO thick films in LPG atmosphere.

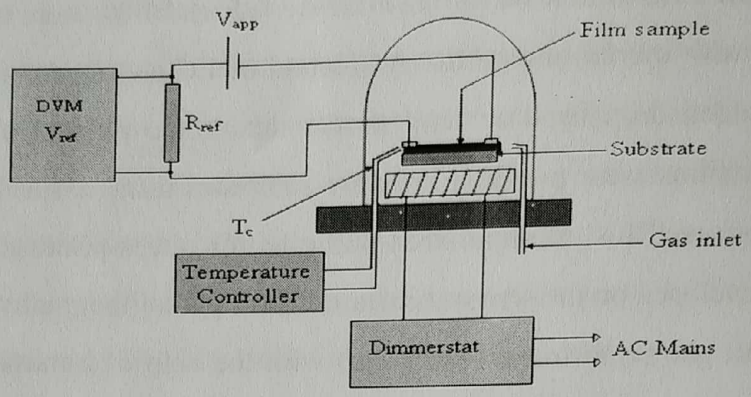


Figure 1. Schematic of static gas sensing system

3. Result and Discussion

3.1 StructuralAnalysis

The crystalline structure of the films was analyzed with X-ray diffractogram in the 20-80^0 (2θ) range using Cuk$_\alpha$ radiation. **Figure 1** shows the XRD pattern of undoped and CuO doped ZnO thick films of different concentrations. The observed phases were for ZnO (ASTM card No. 36-1451) and CuO (ASTM Card No. 5-0661). For 1% and 3% CuO doping, no peak corresponds to CuO phase has observed due to low CuO content. It means CuO may form solid solution with ZnO. For 5% and 7% CuO doping, XRD pattern presents traces of CuO.

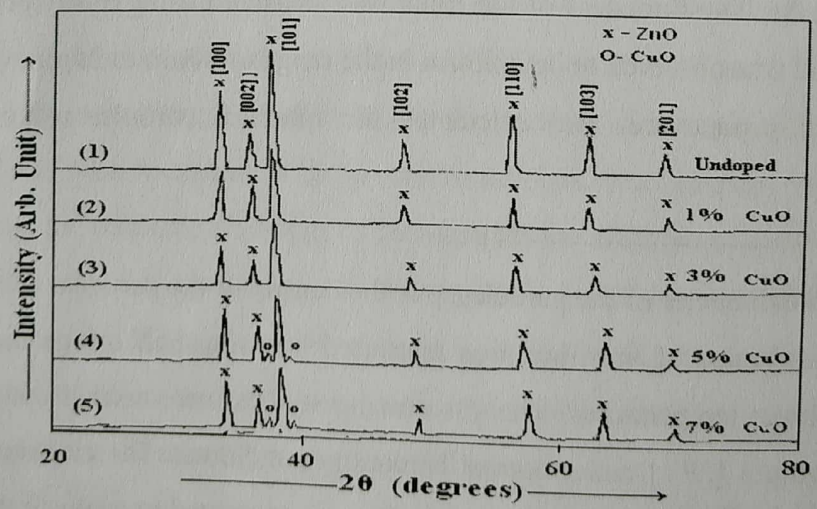


Fig.1 XRD pattern of pure ZnO and ZnO: CuOfilms fired at 450^{o}C

3.2 Surface Morphology Analysis

The gas sensing properties of a metal oxide thick film strongly depends on its morphological features. A high surface area facilitates the chemisorptions process by increasing the adsorption and desorption rates[30].**Figure 2** indicates the SEM images of pure and x wt. % of CuO (x = 1, 3, 5 and 7 wt. %) doped thick films. **Fig. 2-(a)** shows the microstructure of pure ZnO thick film. It showed that the microstructure is nearly uniform with negligible open porosity. **Fig.2-(d)** shows the microstructure of 5% CuO doped ZnO thick film which was most sensitive. It showed that the grain size decreases giving large effective surface area. The larger surface area gives more response to react with the target gas. The film seems to be highly porous for oxygen adsorption. The specific surface area was calculated by using equation 1.The specific surface area increases as the size of the grains decreases [31].

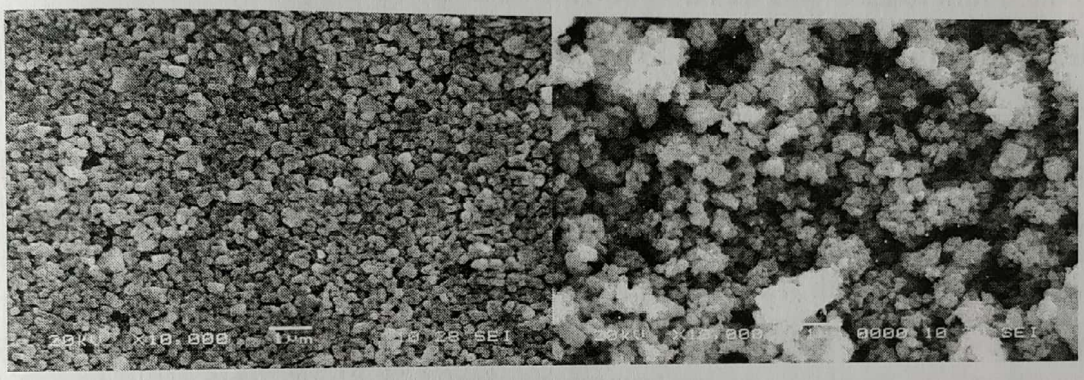


Fig.2a.SEM of Pure ZnO film

Fig.2b.SEM of 1 wt. % CuO: ZnO film

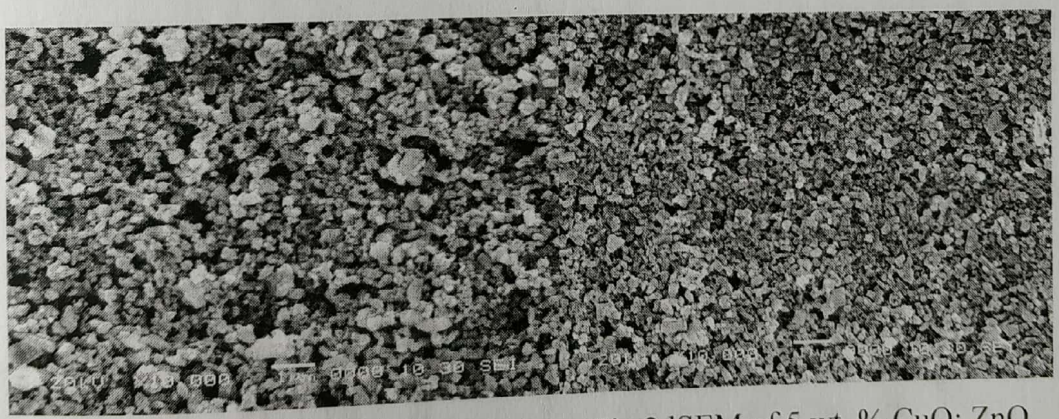


Fig.2c.SEM of 3 wt. % CuO: ZnO film

Fig.2dSEM of 5 wt. % CuO: ZnO

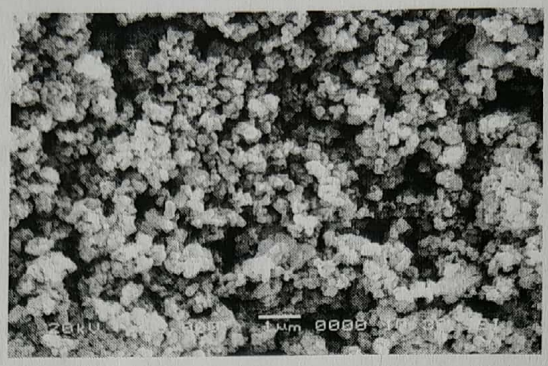
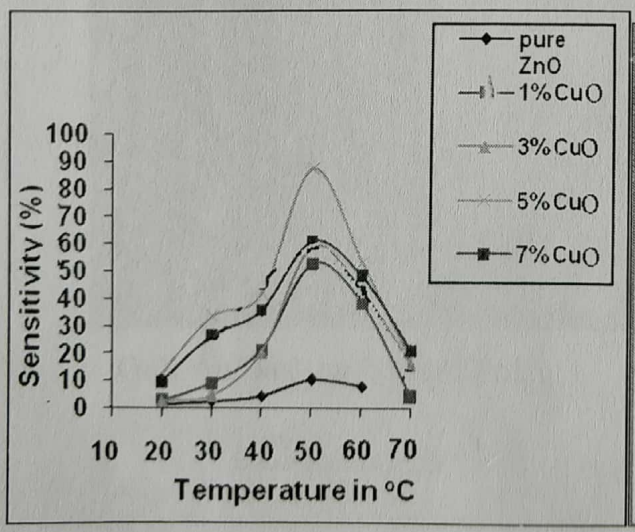


Fig.2e.SEM of 7 wt. % CuO: ZnO

3.3. Gas – sensing characteristics

Figure 3shows the gas sensitivity of pure ZnO and different wt. % CuO doped ZnO thick films fired at 450°C exposed to 1000 ppm of LPG with operating temperatures. The sensitivity of pure ZnO thick film to LPG was found to be 10.5 % at Room temperature (50°C). Pure ZnO is notably less sensitive than doped ZnO.The sensitivity of 5 wt. % CuO doped ZnO film wasobserved to be 88.88% at Room temoerature (50°C) which is higher than other dopant concentrations. **Fig. 4** shows histograms indicating the selectivity of 5wt. % of CuO doped ZnO thick film for different gases against LPG. **Figure 5** shows the variation of sensitivity of the 5% CuO doped ZnO film with LPG concentrations (in ppm) at Room temperature (50°C) temperature. The response and recovery times of 5wt. % CuO doped ZnO thick films are represented in **Figure 6**. The response was quick (~ 08 sec) to 1000 ppm of LPG while the recovery time was fast (~ 17 sec).



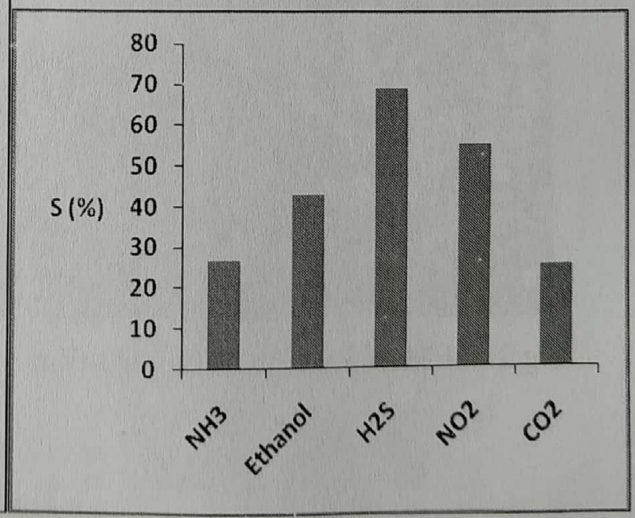


Fig.3 Gas sensitivity of pure and CuO doped filmfor films for 1000 ppm LPG

Fig.4 Selectivity of 5wt. % CuO: ZnO different gases against LPG

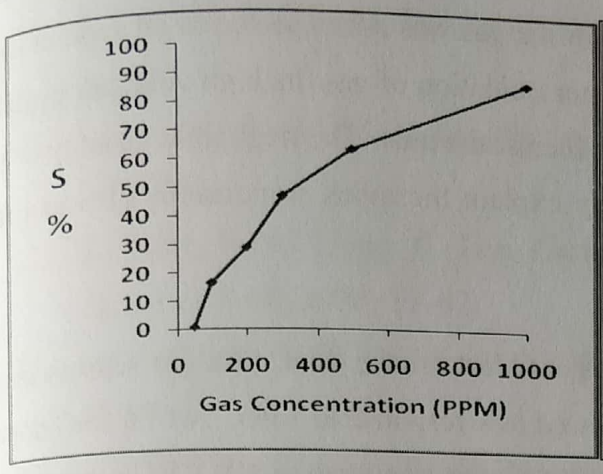


Fig.5.Variation of gas Sensitivity with gas conc.

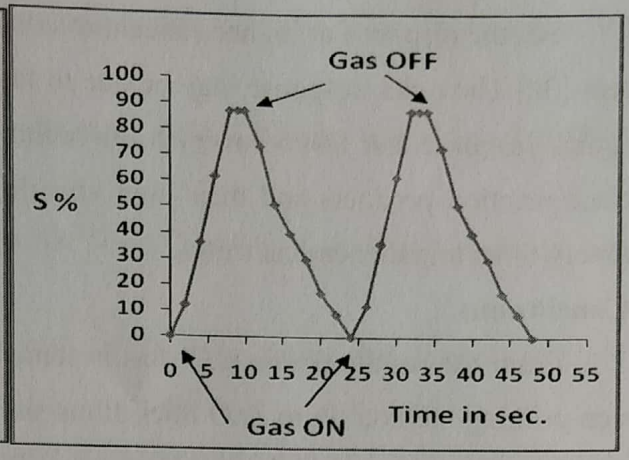


Fig.6 Response and recovery time of 5% CuO doped ZnO film

The higher response may be attributed to the optimum porosity and largest effective surface area available to react with the gas. The response could be attributed to the adsorption–desorption type of sensing mechanism. The amount of oxygen adsorbed on the surface would depend on the number of CuO misfits to adsorb the oxygen which in turn would oxidize the exposed gas.

When the optimum amount of CuO (5 wt. %) is incorporated on the surface of the ZnO film, CuO species would be distributed uniformly throughout the surface of the film. As a result the initial resistance of the film is high and this amount would also be sufficient to promote the catalytic reaction effectively and the overall change in the resistance on the exposure of LPG leading to an increase in the sensitivity. When the amount of CuOon the surface of the film is less than the optimum, the surface dispersion may be poor and the sensitivity of the film is observed to be decreased since the amount may not be sufficient to promote the reaction more effectively. On the other hand, as the amount of CuOon the surface is more than the optimum, the CuO atoms would be distributed more densely. Therefore the initial resistance of the film would decrease and the overall change in the resistance on the exposure of LPG would be smaller leading to lower response [28].

These films were exposed to different gas concentrations of LPG. The sensitivity values were observed to have increased continuously by increasing the gas concentration up to 1000 ppm. The response was highest for 1000 ppm of LPG. The monolayer of the gas molecules formed on the surface could cover the whole surface of the film. The excess gas molecules would remain idle and would not reach the surface active sites of the film.

So, the response at higher concentrations of the gas was not expected to increase in large extent [30].The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status. The negligible quantity of the surface reaction products and their high volatility explain the quick response to LPG and fast recovery to its initial chemical status.

4. Conclusions

From the results obtained, it has become possible to make thick film gas sensors using screen printing method. Pure ZnO thick films showed low response to LPG. 5wt. % CuO doped ZnO thick films showed highest response to LPG at Room temperature (50^0C).The sensitivity increases in proportion to the test gas concentration. The sensor has good selectivity to LPG against NH3, H_2S, Ethanol, CO_2 and NO_2 at Room temperature (50^0C). The sensor showed very rapid response and recovery to LPG.

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