

STUDY OF COMPOSITE METAL OXIDES GAS SENSORS FOR EFFICIENT CARBON DIOXIDE GAS SENSING DEVICE

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ABSTRACT: During study an effectiveness of gas sensing properties of MOS gas sensors, some parameters viz. sensitivity and stability plays very crucial role. These two parameters of the metal oxide semiconductor gas sensor depends on the temperature of the gas detector. Most of the metal oxide based gas sensors operate above the room temperature extending up to many hundred degrees centigrade and it's essential to understand the precise operating temperatures of those sensing elements. to realize good sensitivity stability, one should know and operate these elements accordingly. In present work we prepared a thick film of CuO metal oxides doped with ZnO and design CO₂ gas sensor. Thick film prepared by using screen printing technique and analysed by SEM. It was observed that, in optimized case of 75ZnO:25CuO, the sensitivity increases progressively with temperature and becomes less steady at higher temperature values. From linear dependency, it deviates to a maximum value and beyond now the sensitivity falls rapidly, such behavior is being exhibited by most the metal oxide-based gas sensor. By study it proves that, Role of composite 75ZnO:25CuO metal oxide semiconductor gas sensors is extremely useful for effective CO₂ gas sensing mechanism as compared to Pure ZnO and CuO.

Index Terms - CuO, ZnO, Metal Oxide Semiconductor (MOS), CO₂ gas sensor.

1.0: Introduction:

It is documented that the sensing properties of metal oxide based material depend upon its chemical and physical characteristics, which are strongly passionate in to the preparation conditions, dopant and grain size. this suggests that the synthesis of the sensing material may be a key step within the preparation of high-performance Metal oxide semiconductor (MOS) gas sensors. CuO powders and films are often prepared by synthesis methods [1]. DC-electrical resistance of the films CuO doped with PANi sensor, measured in presence of humidity and these sensors are found to be good sensing materials for humidity. This investigation mainly deals with the preparation of CO₂ gas sensor in CuO doped Polyaniline.

It had been found that CuO system with Polyaniline shows more sensitivity to 60 ppm of CO₂ gas concentration even at temperature. A gas sensor is a device, which detects the presence of various gases in an environment, especially those gases which may be harmful to living animals. The planning of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. Copper oxide (CuO) and Zinc Oxide (ZnO) based chemiresistors have high gas sensing response as compared to the chemiresistors supported conducting polymers but they're operated at heat (>200 °C). Whereas conducting polymer-Polyaniline (PANi) doped with metal oxides sensors have shown better sensing response at temperature [2,3]. Chemical synthesis of CP is typically performed by such oxidants as FeCl₃ and is usually used for the preparation of CP solutions, while electrochemical deposition is employed mainly for deposition of CP films on conducting substrates. A plus of this method is that the possibility to regulate the film thickness by the charge skilled the electrochemical cell during the film growth. Other popular techniques for depositing thin films on various substrates are spin coating by an answer of a chemically synthesized CP, the deposition of 1 or more monomolecular layers of CP by Langmuir-Blodgett technique, or coating of substrates by bilayers of CP and opposed charged polymers by the layer-by-layer technique. CP's are multifunctional materials; it had been not always possible to form a particular separation of their functions. Finally, the appliance of a combinatorial approach for synthesis and high-throughput screening of chemo-sensitive properties of CP is discussed. Polyaniline (PANI) is one such polymer whose synthesis doesn't require any special equipment or precautions. Conducting polymers generally show highly reversible redox behavior with a clear chemical memory and hence are considered as prominent new materials for the fabrication of the devices like industrial sensors. The properties of conducting polymers depend strongly on the doping level, protonation level, ion size of dopant, and water content. Conducting PANI is ready either by electrochemical oxidative polymerization or by the chemical oxidative polymerization method. The emeraldine base sort of PANI is an electrical insulator consisting of two amine nitrogen atoms followed by two amine nitrogen atoms. PANI (emeraldine base) are often converted into a conducting form by two different doping processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base corresponds to the protonation of the amine nitrogen atoms during which there's no electron exchange. In oxidative doping, emeraldine salt is obtained from leucoemeraldine through electron exchanges. The mechanism causing the structural changes is especially recognized to the presence of -NH group within the polymer backbone, whose protonation and deprotonation will cause a change within the electrical conductivity also as within the color of the polymer. Additionally, the nanohybrids-based sensor provides high surface area and abounding reaction sites to accelerate gas diffusion and adsorption as well as the electron transfer. Compare with pristine SnO₂ nanograins alone, the sensitivity of using the nanohybrids increases 7 times for the detection of 50-ppm of H₂S. The response and recovery rate can increase 27 and 22 times at room temperature, respectively. Significantly, this work provides an attractive material for the real-time monitoring of H₂S, whereas the insights into organic-inorganic composite interactions within the sensing mechanism may pave the way for designing functional materials with tailored properties [17]. The synthesis of nanoZnO using two different processes i.e., biological (green synthesis) and chemical synthesis (solution combustion technique). The

prepared materials were characterized by microscopy and spectroscopy techniques, such as Field emission scanning electron microscope (FE-SEM), UV–visible spectroscopy, X-Ray Diffraction (XRD) and Fourier Transform-Infrared (FT-IR) spectroscopy. The two synthesized materials were analyzed and their liquefied petroleum gas (LPG) sensing properties to their sensing characteristics were compared, to highlight the suitable one for chemiresistor. The dynamic gas sensing analysis, sensitivity and resistance were studied. For optimization, sensing characterization was monitored at various operating temperatures in different LPG concentration. Eventually, we found out that the green synthesis route, to fabricate sensor devices is more advantageous as it is cost-effective, eco-friendly and simple[18-25].

2.0: Experimental Method :

2.1: MATERIALS: ZnO,CuO and Al₂O₃ powders (AR grade).

2.2: SENSOR PREPARATION: ZnO,CuO and Al₂O₃ powders (AR grade) were calcinatedat about 725 °C for 4-5 h and were compacted in mortal pestle to get fine powder of the samples.Al₂O₃is used for optimization of local contact formation on screen printed thick film.The ink or paste of the sample was prepared by using screen-printing (thick film technique) technique.These sensors are also known as chemiresistor, metal-oxidebased gas sensor (MOX), gas-sensitive resistors, or semiconductor gas sensors. A sensor element generally comprises a sensitive layer which isplaced on a substrate provided with electrodes for the detecting the signal. The instrument is heated by heater detached from the sensing layer and electrodes by an electrical insulating layer. Among these sensor types, semiconductor-based chemiresistor sensors are broadly used for identification of toxic and combustible gases due to their low cost and simplicity. The binder for screen-printing was prepared by thoroughly mixing 8 wt% butyl carbitol with 92 wt% ethyl cellulose. The powder of EC was mixed thoroughly and BCA was added drop by drop to get the proper viscosity of the paste. The ratio of active powder to binder was kept as 3:7. Also ratio of EC and BCA was kept 8:92.On chemically cleaned glass plate, paste of Al₂O₃ was screen printed and it was kept for 24 hr to dry it at room temperature and then heated at 140⁰C for 2.5 h to remove the binder.The DC power supply (V) in series with resistor ($R_{ref} = 1M\Omega$) is connected to sensor. The voltage drop (Vs) across the R_{ref} is measured by the microvoltmeter. The conductance of the sample (high resistance) was determined by using the half bridge method.

The Al₂O₃ layer provides mechanical support as well as high thermal conductivity. Paste of ZnO and CuO mixed in proper stiochometry, then screen printed on Al₂O₃ layer. Again plate was dried at room temperature for 24 hr and binder was removed by heating it at 150⁰C for 2.5 hr [16].

Finally on the top surface of the sensor, interdigitated electrodes were fabricated using conducting silver paste as shown in the following Figure 1 (b). Thickness of CuO doped with ZnO layer is measured. Optimized sample of 75ZnO:25CuO were characterized by SEM.

To measure the sensitivity, electrical resistance was measured with the help of voltage drop method, best one.

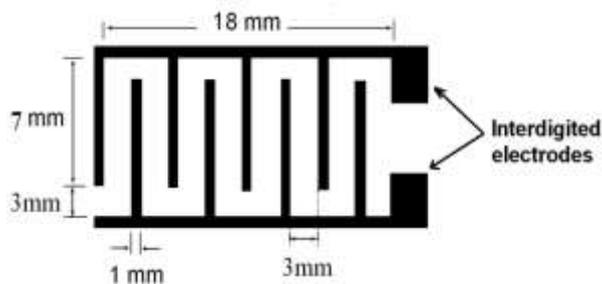


Figure 1 (a) Fabrication of inter digitated Electrodes



Figure 1(b) Actual photograph of interdigitated electrodes.

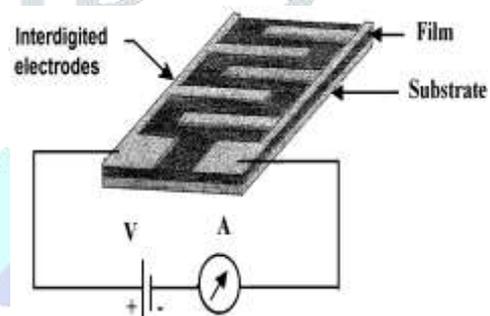


Figure 1 (c) Circuit of resistance measurement using interdigitated electrodes.

3.0: CHARACTERIZATION:

3.1: SEM analysis of 75 ZnO:25CuO:

From SEM, it is confirmed that the crystallite size of 75ZnO:25CuO is smaller than pure CuO and ZnO, it is more porous and hence has greater surface area and therefore shows greater response to CO₂ gas. SEM analysis also confirmed the surface morphology

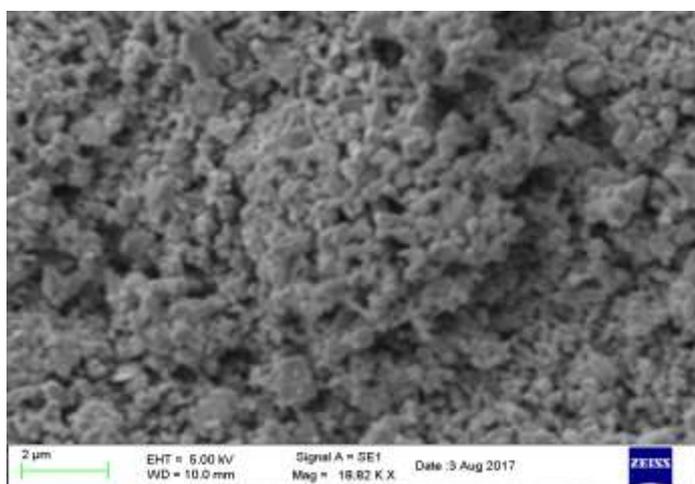


Figure 2(a): SEM analysis of 75 ZnO:25CuO

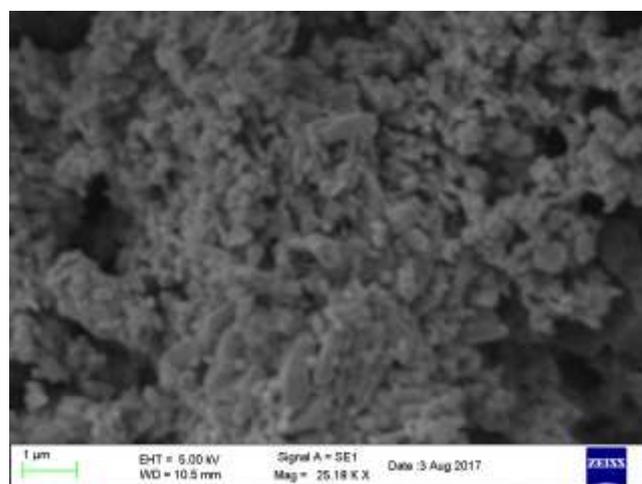


Figure 2(b): SEM analysis of 75 ZnO:25CuO

From above figure 2(a) and figure 2(b) of SEM images it is also observed that 75ZnO:25CuO is porous in nature with average diameter of pore is around 450 nm. In some section of SEM images confirmed some fine voids over them which helps to enhance gas sensing properties.

3.2: Sensitivity for ZnO-CuO System

The sensitivity of the sensor is given by equation (1),

$$S = \left(\frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{air}}} \right) = \left(\frac{\Delta R}{R_{\text{air}}} \right) \quad \text{-----(1)}$$

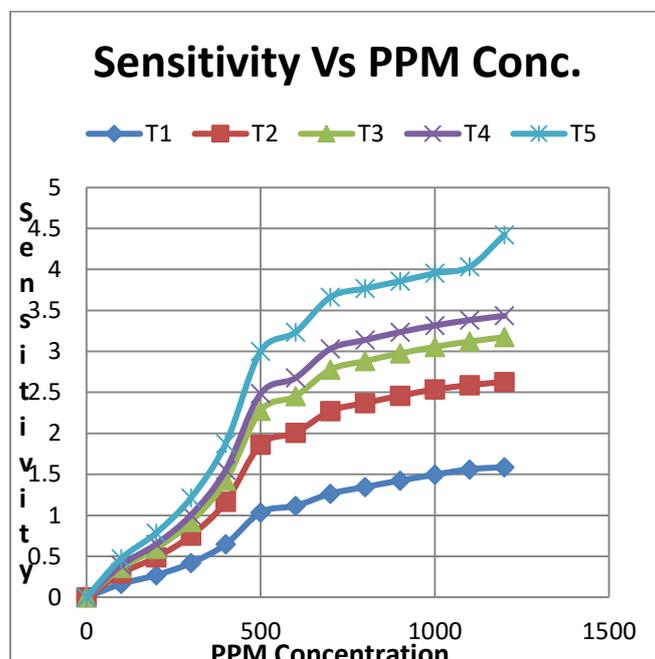
Where, R_{air} and R_{gas} are the resistances of sensors in air and gas respectively.

Following table no.1 reports the maximum sensitivity at 700ppm CO₂ gas concentration, optimized operating temperature, air resistance and resistance per ppm.

From this data it is seen that maximum sensitivity is observed at room temperature 30⁰C. The sensitivity at room temperature is calculated and it is maximum i.e 3.36 for 75ZnO:25CuO sample.

Table No.1: Sensitivity at different compositions of ZnO:CuO

Sr.No.	Sample composition Wt %	Series	Maximum sensitivity at 700 ppm of CO ₂ gas
1	75ZnO:25CuO	T5	3.36
2	55ZnO:45CuO	T4	3.02
3	35ZnO:65CuO	T3	2.77
4	Pure ZnO	T2	2.27
5	Pure CuO	T1	1.26



Graph:1: Sensitivity for T₁,T₂,T₃,T₄ and T₅ samples at various concentration of CO₂ gas.

4.0: CONCLUSION:

From SEM, it is concluded that the crystallite size of 75ZnO:25CuO is smaller and it is more porous and hence has greater surface area and therefore shows greater response to CO₂ gas. SEM analysis confirmed the surface morphology. Screen printing technique is the easiest for the preparation of sensor. 75ZnO:25CuO sensor shows good sensitivity than pure samples ZnO and CuO. From SEM images it is also observed that 75ZnO:25CuO is porous in nature with average diameter of pore is around 450 nm.

5.0: ACKNOWLEDGEMENT:

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