IJRAR.ORG E-ISSN: 2348-1269, P-ISSN: 2349-5138
INTERNATIONAL JOURNAL OF RESEARCH AND ANALYTICAL REVIEWS (IJRAR) | IJRAR.ORG
An International Open Access, Peer-reviewed, Refereed Journal

Study of CO_2 sensing properties of SnO_2-CuO thick films

A. V. Kohale

Department of Physics, Shri R. R. Lahoti Science College, Morshi- 444 905 India

Abstract

The different properties of SnO_2-CuO thick film semiconductor gas sensor in presence of CO_2 gas is studied at room temperature (303 K). The tin oxide and copper oxide (SnO_2:CuO) mixed powder heated at 800^0C. From these active powder thick films was prepared by screen printing technique on glass substrate. The prepared thick film samples were fired in muffle furnace for 1h at 150^0C for removing binder. The electrical behavior of SnO_2-CuO films depends on CO_2 gas. The variation of electrical resistance at room temperature with increasing CO_2 concentration in range 0 to 1100 ppm was measured. The sensitivity is calculated at different CO_2 concentration and presented as response curve. The gas sensor sensitivity increases linearly with increment of the gas concentration of CO_2. From desired study of properties of sensor it is observed that the best material for CO_2 gas detection is $50SnO_2$-50CuO. From the XRD analysis it is observed that the cassiterite tetragonal phase for SnO2 and tenorite monoclinic phase for CuO is observed and crystallite size by using Scherrer formula is found to be 108.5, 97.3 and 122.1 nm for $80SnO_2$-20CuO, $50SnO_2$-50CuO and $20SnO_2$-80CuO respectively. From calculated value seen that the crystallite size is small for $50SnO_2$-50CuO sample in a SnO_2-CuO system and hence it gives higher sensitivity than the other sample.

Keywords: SnO_2-CuO, Screen-printing technique, XRD, CO_2 gas sensor.

1. Introduction

Monitoring CO_2 gas in the atmosphere is important because it is known as a greenhouse gas contributing to global warming. Moreover, decreased oxygen and increased CO2 concentrations reduce the respiration rate of fruit. Control of carbon dioxide gases in modified atmospheres packaging (MAP) also plays an important role in the agricultural sector [1].

In view of this, we have prepared thin films of SnO_2 doped with CuO by screen printing technique on glass substrates and their subsequent oxidation in an oxygen atmosphere and tested the CO2 gas response of the thick film element at different concentration of CO2 gas and presented as response curve.

2. Experimental procedure

2.1 Construction of sensor

SnO_2 and CuO are mixed (Sample code: SA_2: 20:80, SA_5: 50:50, SA_8: 80:20) thoroughly in an acetone medium by using a mortal and pestle and then heated at 800^0C in a furnace. The paste used in screen printing was prepared by maintaining inorganic to organic material ratio at 70:30. The inorganic part consists of a mixture of SnO_2-CuO. The organic part consisted of 8% Ethyl cellulose (EC) and 92 % butyl carbitol acetate (BCA). A solution of EC+BCA (in ratio 8:92) was made and added drop wise to the above resultant mixture until proper thixotropic properties of the paste were achieved. The substrate use for the screen printing was cleaned by using distilled water and then acetone. The paste was screen printed on a glass substrate [2], of size 75mm X 25mm. The films were dried at 150 ^{0}C for about 20 min to remove the organic material. The Film was aged for 4 weeks in open air [3] for drying. For the electrical characterization purpose form the electrodes on two sides of thin film by using silver paste. Thickness of the SA_2, SA_5 and SA_8 films was measured by digital micrometer having resolution ± 1 µm and is found to be 10, 18.5 and 31 µm respectively.

2.2 Measurement of gas sensing characteristics

The gas sensing properties of these samples (thick films) were studied in a home built static gas characterization system. The system consists of a base plate with gas inlet, insulator base, glass plate, DC power supply, resistor (Rs), DC millivoltmeter (Systronics type, Model No. 412, ± 1 µV) and chamber (Volume: 24 lit). The base plate, insulator plate and glass plate are placed on one above the other. This whole assembly is kept inside the chamber.

Using silver paste between two sides of thick films forms the electrodes. The DC power supply (V) in series with resistor (Rs = 1 MΩ) is connected to sensor. The voltage drop (Vs) across the Rs is measured by the microvoltmeter. The required gas concentration inside the system is achieved by passing gas through flow meter in the airtight chamber at ambient condition. The samples were tested for a wide range of concentration of CO_2. The sensitivity is calculated by using the formula

$$S = (R_g - R_a) / R_a$$

Where R_a & R_g are the electrical resistances of the sensor in presence of air and gas+air respectively.

3. Results

The thrust for the present work was to study the gas sensing characteristics of SnO_2-CuO thick films. The results obtained are analyzed, discussed and presented in the following part of this section.

3.1 Characterization of film by XRD

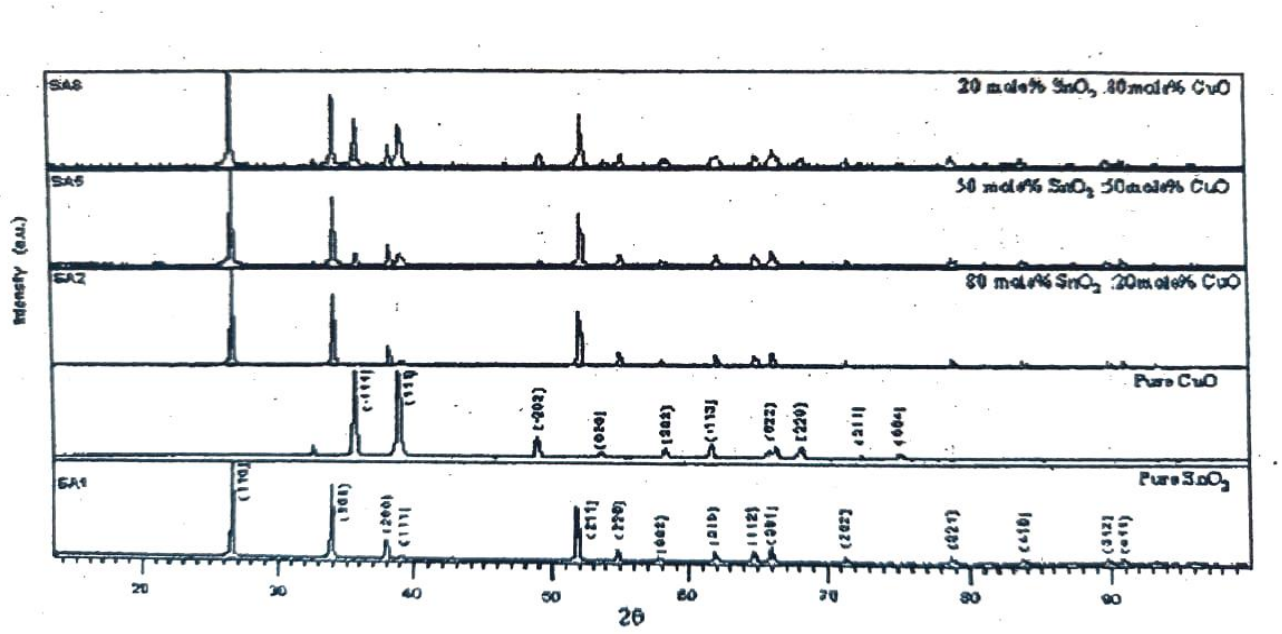

Fig. 1 : XRD patterns of SnO_2-CuO {SA2(80:20), SA5(50:50), SA8(80:20), Pure SnO_2 and Pure CuO} powder

In fig. 1, shows XRD spectra of pure SnO_2, pure CuO and composite of SnO_2 and CuO. The crystallite size for all the samples is calculated by using the Scherrer equation [4]

$$D = 0.9 \lambda / \beta \cos \theta$$

Where D is the crystallite size, k is the constant(= 0.9 assuming that the particles are spherical), λ is the wavelength of X-ray radiation, β is the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average crystallite size of the sample for SnO_2:CuO system for different compositions i.e. 80:20, 50:50, 80:20 is found to be 108.5, 97.37 and 122.1 nm respectively. From this it is observed that the crystallite size for 50 SnO_2- 50 CuO sample is smaller than the other samples.

3.2 Sensing Characteristics of the sensor

To find out the sensor range for the present material the gas concentration-dependent sensitivity was studied systematically for CO_2 gas and results obtained are depicted in fig. 2 shows variation of sample sensitivity as a function of gas concentration for CO_2 gas at room temperature (303 K). From this figure, it is observed that for different compositions of SnO_2 and CuO sensitivity variation is drastically changed. It is observed that the sensitivity is maximum for 50SnO_2-50CuO mixed oxide thick film i.e. 1.325 at 1098 ppm and for other composition i.e. 80SnO_2-20CuO and 20SnO_2-80CuO sample sensitivity is less than the 50SnO_2-50CuO sample.

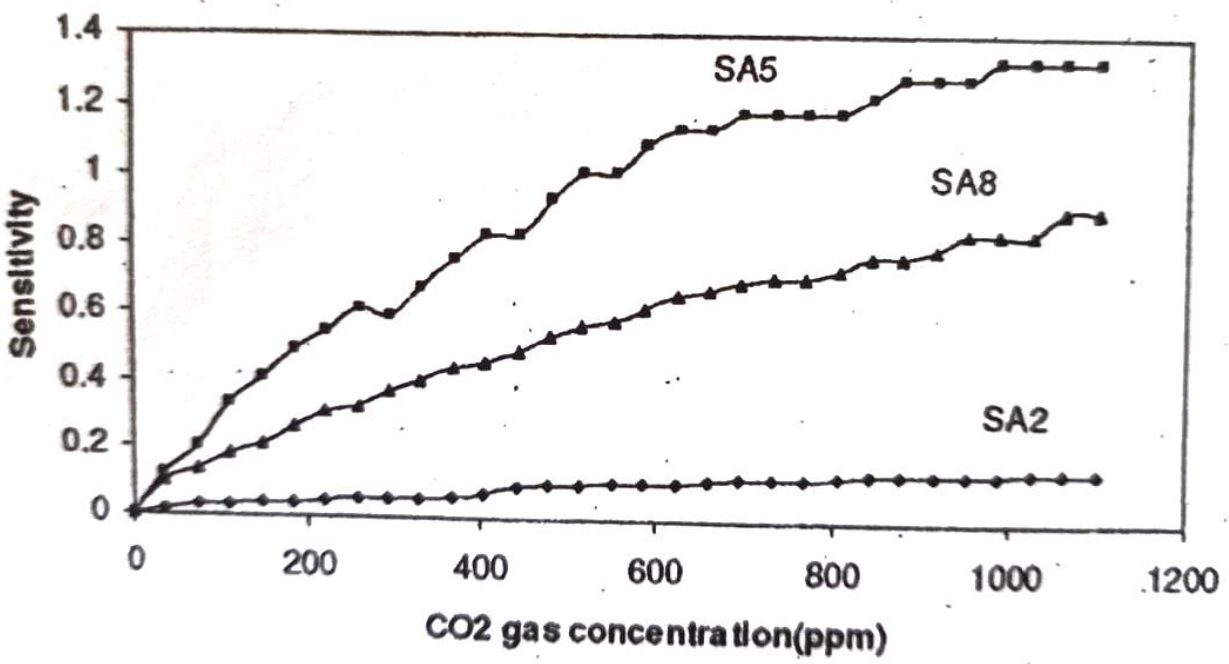

Fig. 2: Variation of sensitivity with concentration of CO_2 gas at room temperature (303 K) for different samples

3.3 Sensing Mechanism

The oxidation state of Copper in SnO2-CuO is important since it influences the interaction with other gas species such as CO_2 [5]. Liu and Robota [6] observed that even under strongly oxidizing conditions, a significant fraction of the copper still remains as cuprous ions (Cu^+). Some Cu^+ ions and oxygen vacancies are located on the surface of the sensing element. When CO_2 gas molecules are brought in contact with the sensing element, they are preferably adsorbed on the Cu^+ sites to form a bond between them due to the existence of an unshared electron pair in oxygen and an empty d orbital in Cu^+. As the electron cloud rearrangement is oriented toward Cu^+ side, which possesses higher electron affinity and eventually broken to release CO and O_2, the bond between oxygen and Cu^+ ions is weakened. The oxygen molecules then recombine with oxygen vacancies through the reaction $\frac{1}{2} O_2 + 2e' + V_o'' = O_0^x$ extracting two free electrons from the conduction band of tin oxide at the same time. This would increase the resistance of the sensing material [7]. In order to correlate morphological properties of the sensors, variation of the crystallite size may play an important role in sensing mechanism. From calculated value seen that the crystallite size is small for $50SnO_2$-50CuO sample in a SnO2-CuO system and hence it gives higher sensitivity than the other sample.

4 Conclusion

Among various metal oxides CuO is a unique promoter of SnO_2 based elements for the detection of CO_2. Typical features of SnO_2:CuO sensors are extremely high sensitivity to CO_2 and very rapid response on switching 'ON' CO_2 and recovery on switching 'OFF' CO_2. The active range of SnO_2:CuO sensor is between 0 and 1098 ppm. The optimum thickness, crystallite size of the SnO_2:CuO sensor is about 18.5 µm, 97.37 nm respectively and the optimum CuO loading seems to be 50 mol%. The $50SnO_2$:50CuO sensor is extremely sensitive to CO_2 gas.

References

[1] S.R. Payne, C.J. Purham, S.M. Scott, C.E. Devine, Mate. Sci. 49 (3), 1998, 277-287

[2] C.A. Harpar, Handbook of Thick Film Hybrid Microelectronics, McGraw-Hill, New York, 1974

[3] S.K. Joshi, C.N.R Rao, N.T. Tsuruto, S. Nagakura (Eds), New Materials, Narosa Publishing House, New Delhi, 1992

[4] J. Tamaki, K. Shiamnoe, Y. Yamada, Y, Yama,oto, N. Miura and N. Yamazoe, Sensors and Actuators B, 49, 1998, 125-186

[5] R. Pirone, P. Ciambell, G. Moretti and G. Russo, Appl. Catal,B, 8, 1996

[6] D.J Liu and H.J. Robota, Appl. Catal,B4, 1994, 155-165

[7] Gong Zhang nad Meilin Liu, Sensors and Actuators B, 69, 2000, 144-152