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# **SnO<sub>2</sub>-WO<sub>3</sub> Mixed Oxide as A Semiconductor Gas Sensor for CO<sub>2</sub>**

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**Abstract:** SnO<sub>2</sub> and WO<sub>3</sub> oxide powders is mixed different composition thoroughly in an acetone medium by using a mortar and pestle and then heated at 900°C in a muffle furnace. The above mixed oxide powder is used to form a thick film by screen printing method. The sensors based on the mixed oxide were used to detect the CO<sub>2</sub> gas at room temperature (303K). The experimental results show that the 45 mol.% SnO<sub>2</sub>-55 mol% WO<sub>3</sub> mixed oxide based sensor exhibits the highest response (sensitivity = 12.45) on 802ppm CO<sub>2</sub> gas at room temperature. The response and recovery time for all the sensors was studied. The average crystalline size was calculated from XRD spectra is ranging from 21.22nm to 23.10nm for mixed oxide powder whereas pure WO<sub>3</sub> is 28.23nm.

**Keywords**—Mixed oxide; screen-printing technique; CO<sub>2</sub> gas; sensitivity; response time; recovery time.

## I. INTRODUCTION

Gas sensors are used for many applications such as process controls in chemical industries, detection of toxic environmental pollutants, and for the prevention of hazardous gas leaks. Different oxide semiconductors such as SnO<sub>2</sub>, WO<sub>3</sub>, ZnO, MoO<sub>3</sub>, TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and mixed oxides have been studied and showed promising applications for detecting target gases such as NO<sub>x</sub>, O<sub>3</sub>, NH<sub>3</sub>, CO, H<sub>2</sub>S and Sox [1–3] The working principle of these sensors is based on the detection of a change in resistance on exposure to a gas. Due to the constraints of gas permeation only the surface layers are affected by such reactions. Among various oxide sensors, WO<sub>3</sub> is responsive to NO<sub>x</sub>, H<sub>2</sub>S, and NH<sub>3</sub> [4–6].

In this study, WO<sub>3</sub> as a main gas-sensing element with a metal oxide of SnO<sub>2</sub> was added in order to stabilize the electrical characteristics. To enhance the sensitivity of the gas sensor to detect gases different mol% of SnO<sub>2</sub> and WO<sub>3</sub> were added. The WO<sub>3</sub> thick film was manufactured based on the screen printing process, which is not only economical but also enables mass production. We studied the optimal conditions of the gas sensor to detect CO<sub>2</sub> through the analysis of the characteristics of gas detection based on the experimental parameters.

## II. EXPERIMENTAL PROCEDURE

### A. Construction of sensor

SnO<sub>2</sub> and WO<sub>3</sub> is mixed (Sample code SA<sub>1</sub>: 20:80, SA<sub>2</sub>:30:70, SA<sub>3</sub>:45:55) thoroughly in an acetone medium by using a mortar and pestle and then heated at 900°C in a furnace. The paste used in Screen-printing was prepared by maintaining inorganic to organic material ratio at 70:30. The inorganic part consisted of a mixture of SnO<sub>2</sub>:WO<sub>3</sub>. 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 used for the screen printing was cleaned by using distilled water and then acetone. The paste was screen printed on an glass substrate [7], of size was 75mm X 25 mm. The films were dried at 150 °C for about 20 min to remove the organic material. The film was aged for 4 weeks in open air [8] for drying. For the electrical characterization purpose form the electrode on two side of thick film by using silver paste. Thickness of the SA<sub>1</sub>, SA<sub>2</sub> and SA<sub>3</sub> films was measured by digital micrometer having resolution ± 1µm and is found to be 12, 13.5 and 15.3µm respectively.

### B. Measurement of gas sensing characteristics

The gas sensing properties of these samples (thick film) were studied in a home –built static gas characterization system. The system consist of a base plate with gas inlet, insulator base, glass plate, Aplap make DC power supply, resistor (Rs), DC Millivoltmeter (Scientific make type ±1µV), and chamber(Volume :12 lit). The base plate, insulator plate and glass plate are placed 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=1MΩ) 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 with flow rate

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200 ml/min in the airtight chamber at ambient condition. The samples were tested for a wide range of concentration of CO<sub>2</sub>. The sensitivity is calculated by using the formula

$$S = \frac{R_g - R_a}{R_a}$$

Where R<sub>a</sub> & R<sub>g</sub> are the electrical resistance of the sensor in presence air and gas+air respectively.

The structure of sensor material was examined by X-ray diffractometer (PANalytical PW: 3040/60 made in Netherland) using CuK $\alpha$  radiation (1.5418 Å) in the 2 $\theta$  range of 5 -100°. The 2 $\theta$  step and step acquisition time were 0.0170° and 7.7523 s respectively.

### III. RESULTS

The thrust for the present work was to study the gas sensing characteristics of SnO<sub>2</sub>: WO<sub>3</sub> thick films. The results obtained are analysed, discussed and presented in the following part of this section.

#### A. Characterization of film by XRD

X-ray diffraction patterns for 20SnO<sub>2</sub>-80WO<sub>3</sub>, 30SnO<sub>2</sub>-70WO<sub>3</sub>, 45SnO<sub>2</sub>-55WO<sub>3</sub>, Pure SnO<sub>2</sub> and pure WO<sub>3</sub> sensors are shown in Fig. 1. The XRD is obtained in terms of 2 $\theta$  and intensity in the range 5-100°. The XRD spectra shows number of peaks suggests the total crystalline behavior of the films. It was investigated that W-O system is rather complex with a large number of phases. From Fig.1, it is observed that XRD-pattern contain nearly 15-18 peaks, out of these, nearly 14-15 peaks are prominent peaks of WO<sub>3</sub>. The tungsten oxide exhibits a cubic perovskite like structure which based on the corners sharing of WO<sub>6</sub> regular octahedral with the W atoms at the centre of each octahedral.

The peaks obtained about 30° is observed in all samples corresponds to WO<sub>3</sub>. In WO<sub>3</sub> five distinct crystallographic modifications takes place between absolute zero and its melting point (1700 K). When temperature is decreased from the melting point, the crystallographic modifications: tetragonal-orthorhombic- monoclinic-triclinic-monoclinic having phases  $\alpha$ WO<sub>3</sub>,  $\beta$ WO<sub>3</sub>,  $\gamma$ WO<sub>3</sub>,  $\delta$ WO<sub>3</sub> and  $\epsilon$ WO<sub>3</sub> respectively forms [9-14]. The observed peaks of SnO<sub>2</sub> having (h,k,l) values (101), (301) and (321) are reflected in all samples and related to the stable state of cassiterite or rutile phase. The lattice parameter values obtained for SnO<sub>2</sub> are a=b=4.7382 Å and c=3.1771 Å with c/a ratio of 0.6725.

These values are in the range 21-23° corresponds to (002), (200) and (106) phases related to WO<sub>3</sub>. Similarly a prominent phase (202) at close agreement with the values reported by Diegnez [15] and Robertson [16,17]. It has been reported that thin films of SnO<sub>2</sub>-WO<sub>3</sub> mixed oxides crystallize in the tetragonal, cassiterite SnO<sub>2</sub> structure with the lattice parameters slightly larger than those for undoped SnO<sub>2</sub>.

This is in agreement with the ionic radii of W<sup>6+</sup> (0.074 nm) and Sn<sup>4+</sup> (0.071 nm). This suggests the substitutional mechanism of W incorporation.

The average grain size can be determined from XRD pattern using Debye-Scherrer formula [18]

$$D = K \lambda / \cos \theta \quad (1)$$

Where  $D$  is the crystallite size,  $K$  is the shape factor, which can be assigned a value of 0.89 if shape is unknown,  $\theta$  is the diffraction angle at maximum peak intensity,  $\lambda$  is the wave-length of radiation and  $\beta$  is the full width at half maximum of diffraction angle in radians. The average crystallite size for these samples is found to be in the range of 21.22nm to 23.10nm. It is observed that the average crystallite size is found to be nearly same for all samples except pure WO<sub>3</sub> sample for which it is 28.23nm. This indicates that the crystallite size of SnO<sub>2</sub>-WO<sub>3</sub> composite decreases.

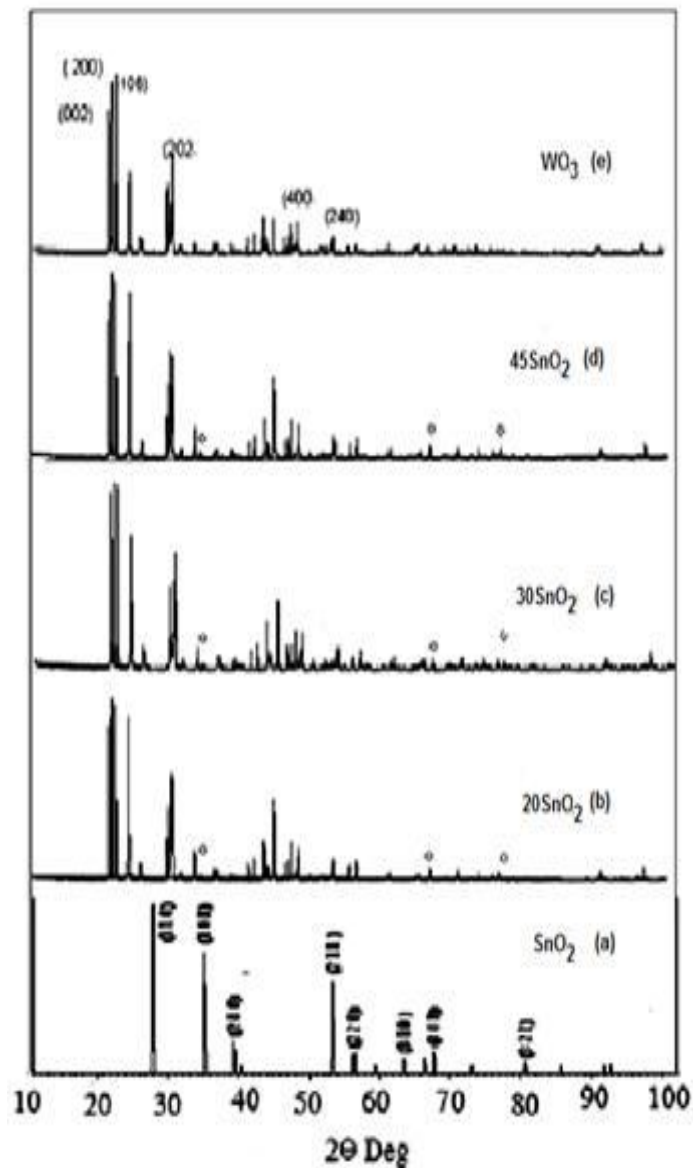


Fig.1. XRD pattern of (a) SnO<sub>2</sub> (b) 20SnO<sub>2</sub>-80WO<sub>3</sub> (c)30SnO<sub>2</sub> -70WO<sub>3</sub> (d) 45SnO<sub>2</sub> -55 WO<sub>3</sub> (e) WO<sub>3</sub> .

**B. Sensitivity of Sensor**

The resistance of the prepared sensors is found to increase with increasing the CO<sub>2</sub> as concentration. The sensitivity of the sensor is calculated by the following formula

$$S = (R_g - R_a) / R_a = \Delta R / R_a . \tag{2}$$

Where *R<sub>a</sub>* is the resistance of the sensor in air and *R<sub>g</sub>* is the resistance of the sensor in CO<sub>2</sub> gas. The sensitivity of these sensors increases linearly with the CO<sub>2</sub> gas concentration at room temperature (303 K). The variation of sensitivity with CO<sub>2</sub> gas concentration at room temperature for various concentration of SnO<sub>2</sub> is shown in Fig.2. It is observed that the sensor 45SnO<sub>2</sub> - 55WO<sub>3</sub> shows highest sensitivity 12.45, while sensor of pure SnO<sub>2</sub> ,pure WO<sub>3</sub> and other composition i.e 20SnO<sub>2</sub>- 80WO<sub>3</sub>,30SnO<sub>2</sub>- 70WO<sub>3</sub> shows least sensitivity to CO<sub>2</sub> gas. In case of 45SnO<sub>2</sub> -55WO<sub>3</sub> sensor the active surface area will be more than the other samples causing more adsorption of gas therefore the sensitivity will be more. As far as the gas sensing is concerned the structural properties are utmost important. In the mixed oxide SnO<sub>2</sub> -WO<sub>3</sub> the porosity of the surface and the active surface area enhance the sensitivity.

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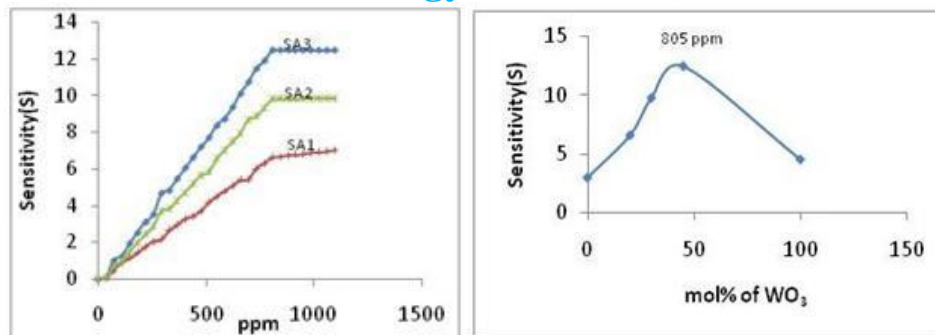


Fig.2.Variation of sensitivity with concentration of CO<sub>2</sub> (ppm) gas at room temperature (303K)  
Fig.3.Variation of sensitivity with WO<sub>3</sub> composition at room temperature for 805ppm of CO<sub>2</sub> gas

TABLE I  
RESPONSE TIME AND RECOVERY TIME OF SENSORS

Sr. No	Composition (mol %) SnO <sub>2</sub> -WO <sub>3</sub>	Response time (s)	Recovery time (s)
1	100-00	137	72
2	80-20	121	413
3	70-30	124	37
4	40-60	109	22
5	00-100	134	86

### IV. CONCLUSION

The sensing properties of thick film pure SnO<sub>2</sub>, 20SnO<sub>2</sub>-80WO<sub>3</sub>, 30SnO<sub>2</sub>-70WO<sub>3</sub>, 45SnO<sub>2</sub>-55WO<sub>3</sub>, Pure WO<sub>3</sub> gas sensors were investigated. The highest sensitivity of about 12.45 was achieved by the SA<sub>3</sub> (45SnO<sub>2</sub>-55WO<sub>3</sub>) sample. From the XRD pattern average crystalline size was found, it shows that crystalline size is less for mixed oxide than the pure oxide. Among all the sample fast response and recovery time was found for SA<sub>3</sub> sample is 109 S and 2 S.

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