STUDY OF SENSING MECHANISM OF CuO and TiO_2 METAL OXIDES FOR CO_2 GAS

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ABSTRACT

The sensing properties of mixed metal oxide-based material depend upon its chemical, physical characteristics and amount of mixing of two metal oxides, which are strongly keen in to the preparation conditions, dopant and grain size. This praises that the development of the sensor thick film is a one of important step within the preparation of good mixed metal oxide semiconductor gas sensors. CuO and TiO_2powders and films are frequently developed by a screen printing techniques. Sensing properties of thick film studied by at different concentration of carbon dioxide gas and also study surface morphology of sample by using SEM. It has also been studied the stability and dynamic response of sensor against sensing gas.

Keywords: *CuO:TiO_2; screen-printing technique; CO_2 gas sensor.*

1. Introduction

The last century has seen increased industrial growth worldwide. A side effect of this development is an exponential increase in pollution of earth, air and water, especially in densely populated areas. While land pollution is locally restricted and great efforts have been made during the last decades to improve the quality of rivers and larger bodies of water, air pollution is not so easily reduced.

Nowadays, there is a great interest in implementing sensing devices in order to improve environmental and safety control of gases. The most used gas sensor devices can be divided in three big groups depending on the technology applied in their development: solid state, spectroscopic and optic.

While spectroscopic and optic systems are very expensive for domestic use and sometimes difficult to implement in reduced spaces as car engines, the so called solid state sensors present great advantages due to their fast sensing response, simple implementation and low prices [1,2,3]. These solid state gas sensors are based on the Change of the physical and /or chemical properties of their sensing materials when exposed to different gas atmospheres. Although the number of materials used to implement this kind of devices is huge, this work was centered in studying the semiconductor properties, in those material using TiO_2 and CuO as sensing materials.

The main purpose of this paper is to study new materials for gas sensing elements starting from the knowledge in thick film production using screen-printing technique.

2. Experimental Work

2.1 Materials

The list of chemicals and materials along with the sources and grades used for the preparation of sensors are given in the table 1.

Table 1: Chemicals and materials with sources and grades

.Chemicals	Acronym	Grade	Source
Copper Oxide	CuO	AR	SD Fine, India
Titanium Oxide	TiO_2	AR	SD Fine, India
Alumina	Al_2O_3	GR	LOBA Chemi, India
Methanol	CH_3OH	AR	SD Fine, India
Acetone	CH_3COCH_3	AR	SD Fine, India
Ethyl Cellulose	$[C_6H_7O_2\ (OC_2H_5)_3]$ n.	AR	SD Fine, India
Butyl Carbitol	$C_8H_{18}O_3$	AR	Merck, India

2.2 Synthesis and Sensor preparation

As mentioned in the aim of the present work, the work concentrates on thick film sensor of CuO-TiO_2. The experimental method for the preparations of materials, fabrication of sensors, effect of dopant, screen-printing method and fabrication of gas chamber and gas flow meter is discussed.

2.3 Synthesis and Sensor preparation

Calcination, the initial heat treatment, the precursor (hydrated metal oxides) undergoes provides thermal energy, which enables the growth of metal oxide particles. An increase in calcination temperature increases monotonously the mean grain size[4].

In addition, the full width half maximum of the grain size distribution also increases monotonously with calcination temperature. A longer calcination time results in larger grains and a broader grain size distribution. Grinding results in a reduction of grain size too. The smallest grains are obtained by grinding before and after the calcination [5].

The powders of TiO_2, CuO and Al_2O_3 were calcinated at 820^0C in an automatically temperature-controlled muffle furnace for 5 to 6 hrs. The powders of these samples were crushed in pestle before after the calcination to get the homogeneity in the powders. The Series of the samples were prepared. The different combinations are shown in table 2.

Table 2: Sample codes and mole percent for series CuO and TiO_2

Sr. No.	Series	Composition of CuO (mole %)	Composition of TiO_2 (mole %)
1	A	100	0
2	B	80	20
3	C	70	30
4	D	60	40
5	E	50	50
6	F	40	60
7	G	30	70
8	H	20	80
9	I	00	100

The ink or paste of the sample was prepared by using screen-printing (thick film technique) [6,7] technique. The standard basic materials: EC (ethyl cellulose), BCA (Butyl Carbitol Acetate) were used for the screen-printing process [8,9].The EC and BCA were used as binders. The active powder and Ethyl cellulose were mixed thoroughly. During this mixing process, the BCA was added drop by drop to obtain the proper viscosity of the paste. For thixotropic property for printing on the substrate, the ratio of active powder to binder was kept as 3:7. Also ratio of Ethyl cellulose (EC) and Butyl Carbitol acetate (BCA) is kept at 8:92.

The glass substrate of size 7.5 x 2.5 cm^2 was used. The substrate is an important part of any thick-film process. It must also be proper shaped. For normal electronic purpose, the substrates structure should be rectangle. These dried samples were further heated at 140°C for 50-60 minutes with a heating and cooling rate of 22°C/min to remove binder. The thickness of all the prepared sensor samples was measured by digital micrometer. And following gas chamber (Figure 1) is used for characterization.

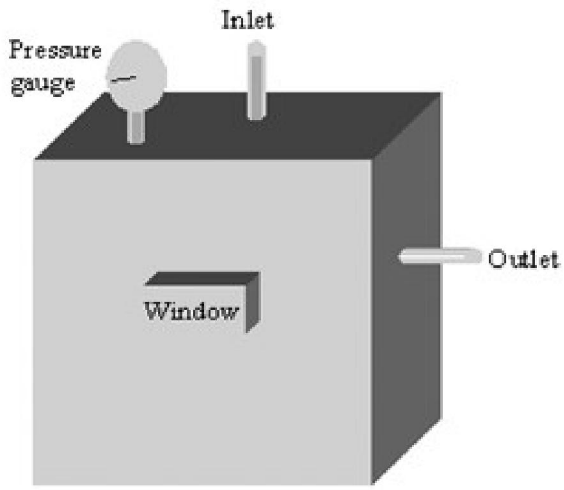

Figure1: Gas chamber for CO_2

3. Result and Discussion

3.1 Gas sensing properties of CuO: TiO_2 composites-

The variation of sensitivity of sensors of pure and CuO:TiO_2 composite materials with concentration of CO_2 gas at room temperature as shown in following Figure 2.

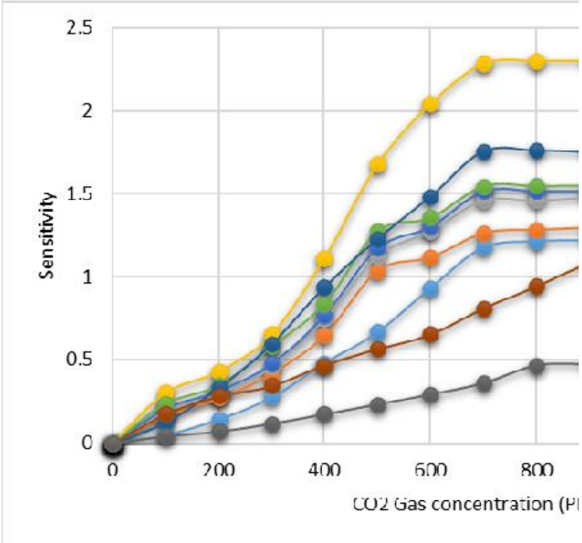

Figure 2: Variation of sensitivity of pure CuO, pure $TiO_2$and CuO: TiO_2 composites with CO_2 gas concentration (ppm) at room temperature (300K).

From above Figure shows that the sensitivity increases linearly upto 900 ppm and beyond that it shows saturation. Sensitivity of 60CuO:40TiO_2 composite has found maximum value i.e. 2.30 at 900 ppm as compare to other composites.
It is also observed that with decreasing concentration of doping of TiO_2in CuO:TiO_2 composites, the sensitivity increases and becomes maximum for 60CuO:40TiO_2 composite. For pure CuOand TiO_2 sensitivity is less as compare to 60 and 40 composition. It is due to the high porosity of 60CuO:40TiO_2 composite as compared to other and pure CuO and TiO_2. Thus active surface area may available due to high porosity.

3.2 Dynamic response

Dynamic responses of CuO:TiO_2 series for 300 ppm, 600 ppm and 900 ppm are shown in the following Figure.

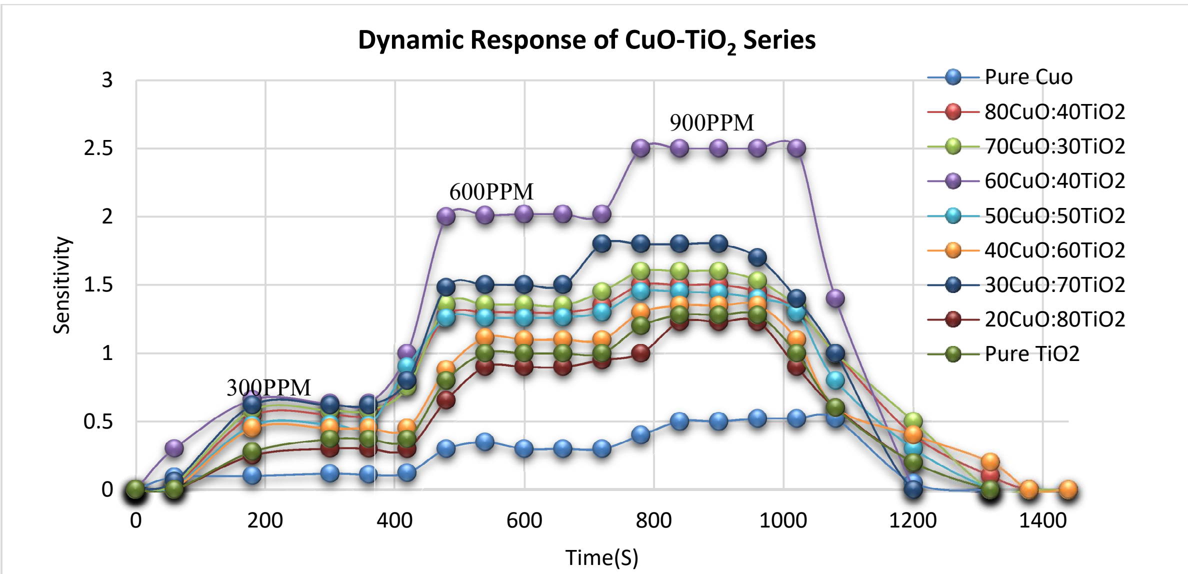

Figure3:Dynamic response of pure and composite sensors at 300, 600 and 900 ppm of CO_2 gas concentration at room temperature (303 K).

From above Figure, it is observed that $60CuO:40TiO_2$ sensor sensor shows fast recovery as compared to other composition sensors therefore $60CuO:40TiO_2$sensor is the best among the various reported sensors.

3.3 Stability of Sensor

Sensor stability is expressed in terms of measurement of resistance with time and shown in Figure. 4. It is defined as the change in resistance of sensor with time **[10,11]**.

The resistance values of optimize sensors $60CuO:40TiO_2$, measured with time at room temperatures are listed in the table 4.4 for time 60 h.

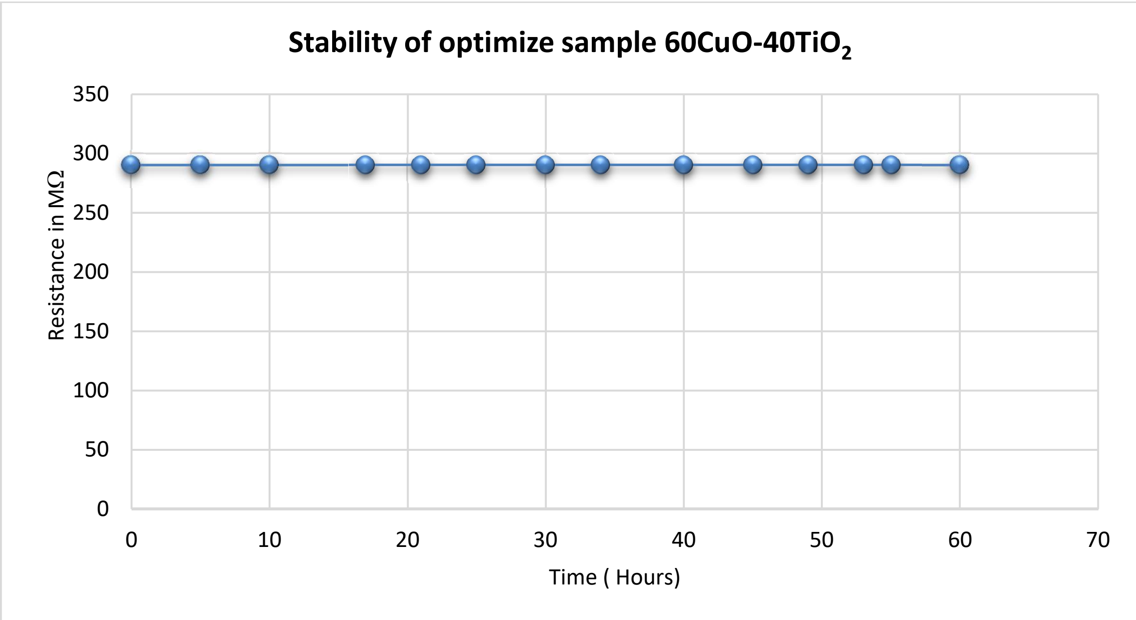

Figure 4: Stability curve

Table 3: Change in resistance of sensors in air with respective time.

Time (hour)	**Sensor resistance in air (MΩ)**		**Time (hour)**	**Sensor resistance in air (MΩ)**	
	$60CuO:40TiO_2$			$60CuO:40TiO_2$	
0	290.1491		34	290.1491	
5	290.1491		40	290.1491	
10	290.1491		45	290.1491	
17	290.1491		49	290.1491	
21	290.1491		53	290.1491	
25	290.1491		55	290.1491	
30	290.1491		60	290.1491	

From the Figure 4 and table 3, it is observed that all the sensors are stable for long-time use.

3.4 SEM Analysis

The surface morphology of optimized sample$60CuO:40TiO_2$ material was studied by SEM and its picture is shown in the following Figure.5

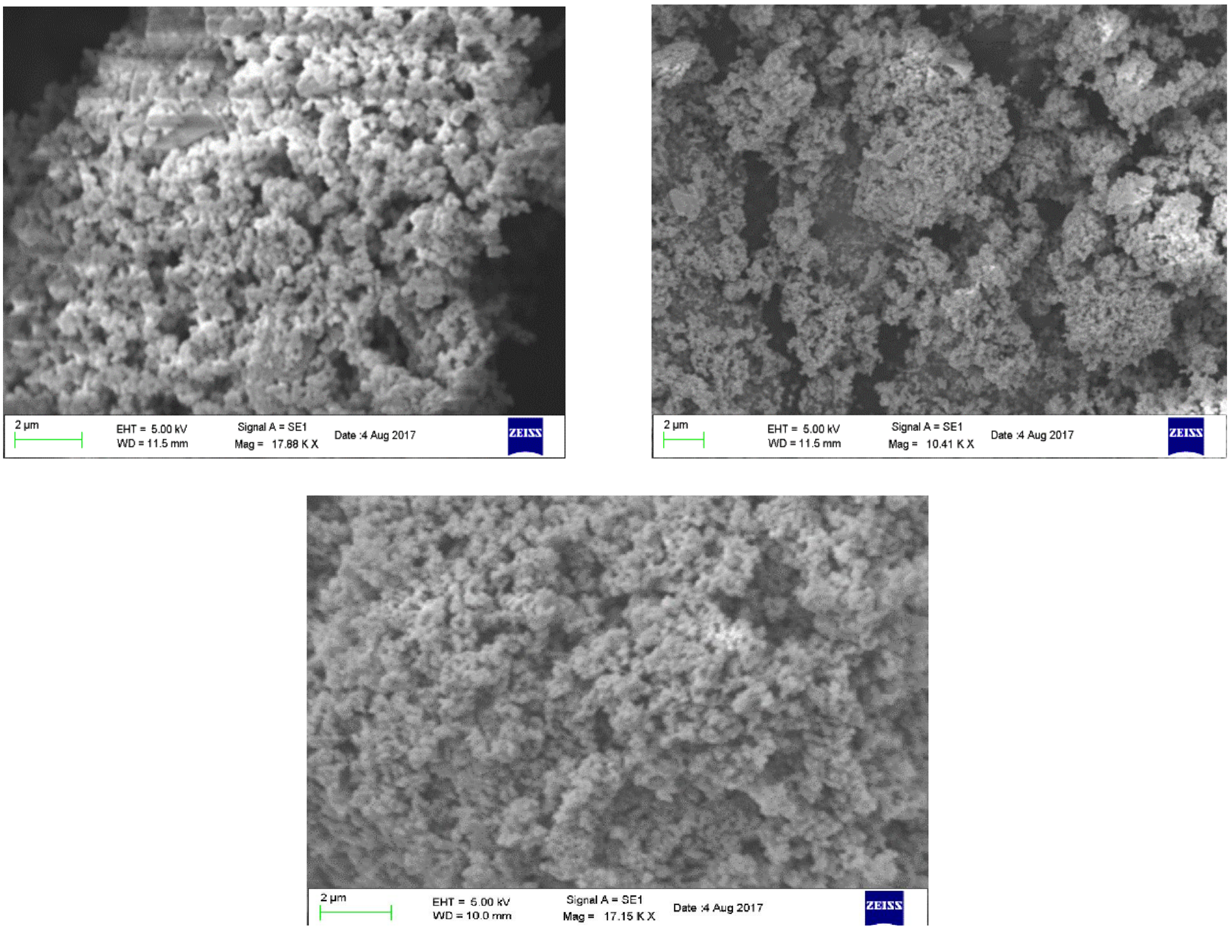

Figure 5: SEM pictures of 60CuO:40TiO_2at different magnifications

The surface morphologies of 60CuO:40TiO_2studied and the average diameter and number of pores per inch composites are 250& 115respectively. And number of pores per inch for pure and other composites is less.

It is also found that average diameter of pore in case of 60CuO:40TiO_2 composition is small as compared to other compositions. This also tends to exhibit large surface area and high response of the sample [12-18].

4. Conclusion

We observed that due to grinding and calcination, the grain size of metal oxide power can be improved. Calcination is initial heat treatment, the precursor undergoes provides thermal energy, which enables the growth of CuO and TiO_2 metal oxide particles. A longer calcination time results in larger grains and a broader grain size distribution. Grinding results in a reduction of grain size too. The smallest grains are obtained by grinding before and after the calcination.

If the grains are smaller than surface area will be larger. The sensitivity towards test gases increases due to increase in surface area. Thus, the calcination of metal oxide powder before paste preparation of film enhances the sensitivity.

From analysis of SEM, it is analyzed that the crystalline size of optimized sample 60CuO:40TiO_2 is smaller as compared with pure CuO and TiO_2. Also observed that, optimized sample is more pores and hence has large surface area as compare to other combination. It has been also observed that enhancement in gas (CO_2) response for optimized sample 60CuO:40TiO_2 as compare to other composition. SEM analysis confirmed the surface morphology. From dynamic response and stability graphs, it has been observed that optimized sample shows good sensitivity and stability.

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