THICK-FILM NANOSIZED METAL OXIDE SnO_2 DOPED WITH Y_2O_3 FOR GAS SENSING APPLICATIONS

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ABSTRACT

This paper presents the preliminary investigation on the response of thick-film gas sensitive sensors based on mixed nanosized metal oxide Cu2O-Y2O3-SnO2. Different ratio of the powders composition were mixed and printed onto the electrode of the prepared sensors. Samples were tested in present of methane and Liquefied Petroleum Gas (LPG) in different temperatures from 50°C to 300°C of heater, and the response and recovery times were compared with undoped film.

Keywords: *gas sensor, metal oxide nanosize composition, thick-film sensor*

INTRODUCTION

Numerous solid state gas sensors based on tin oxide have been reported. A wide band gap (3.6 eV at 300 °K [1]) as an n-type semiconductor material has established a widely used of tin oxide as sensing elements in gas sensors [2]. The principal advantages of these sensors are: ease of use, robustness, low-cost and the possibility of in-situ control and monitoring.

The adsorption of the surface of thick-film gas sensors based-on SnO2 is strongly affected by the preparation of active layer, which determines the sensitive material, grain size, density, and surface structure. The synthesis of different doping material into tin oxide has reported by the researches [3] – [8]. Ytrria (Y2O3) with band gap of 4.54 eV [9] is used to make the high temperature superconductor such as YBa2Cu3O7, known as "1-2-3" to indicate the ratio of the metal constituents:

$$0.5Y2O3 + 2BaO + 3CuO + 0.25O2 \rightarrow YBa2Cu3O7 \quad (1)$$

Ignoring copper oxide yields barium ytrrite tetroxide:

$$0.5Y2O3 + 2BaO + 0.25O2 \rightarrow YBa2O4 \quad (2)$$

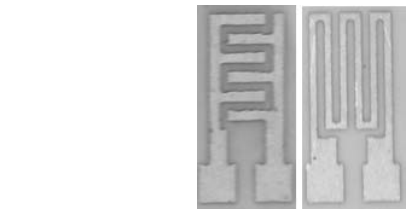
This synthesis is typically conducted at 800 °C with metal oxidized semiconducting properties [9]. Furthermore adding 5 to 10 percent of yttria in ratio causes to reduce the grain size of the nano particles of crystal and gives more stabilization of thermal resistance shock and mechanical strength to the deposited film layer [10]. Replacing barium oxide with tin oxide yields tin yttrium hexoxide:

$$2[0.5Y2O3 + 0.5SnO2 + 0.25O2 \rightarrow Sn0.5YO3] \quad (3)$$

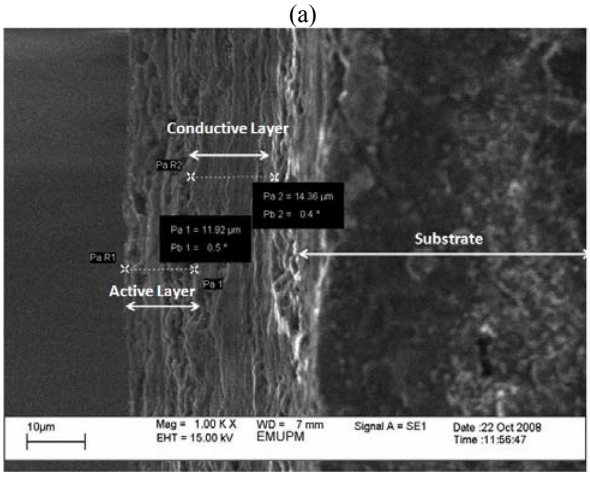
In this work different ratio of Ytrria were doped into SnO2 and the prepared powder was mixed with an organic binder to be used as active layer. The paste then printed onto electrodes and characterization of the films was investigated using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX).

EXPERIMENTAL WORKS

A platinum paste (ESL-5545) was used to print a heater and interdigitated electrode patterns onto each side of a 250μm thickness alumina substrate (ADS996-STD), using printing screen machine (DEKJ1202RS). The films were left at room temperature, dried at 150°C and finally fired at 980°C; for 10, 12, and 15 minutes respectively. The thickness of the platinum films was measured using an optical microscope by means of a cross section cutting with an average of thickness about 15μm (Figure 1).



(a)



(b)

Figure 1: (a) Electrodes (left) and Heater (right) of Sensor, (b) Conductive and Active layers

A binder was prepared by 5 hours mixing 5wt% Ethyl Cellulose and 95wt% α-Terpinoel at 40°C. Three different metal oxides composite, 95%wtSnO2-5wt%Y2O3, 90%wtSnO2-10wt%Y2O3 and 85%wtSnO2-15wt%Y2O3 were ultrasonically mixed for 12 hours in present of acetone as media and ground in a ball mill for 48 hours. The powders then were dried to vaporize the media in an oven and sintered at 800 °C for 4 hours. The sintered powders then mixed with drops of binder into an agate mortar to give a good viscosity to the paste. A thick layer of the prepared pastes with average of 12 micron was printed onto the electrode of the samples (Figure 1b), left at room temperature, dried at 150°C and fired at 850°C for 10 minutes.

RESULTS AND DISCUSSIONS

Microscopic Analysis

Surface of the films was analyzed in order to observe the porosity of the surface, crystalline formation, thickness, and material composition. The thickness average of the active layer printed onto the electrodes was measured using SEM from cross section cutting of the sensor. Figure 1b shows an average of 12 µm of active layer thickness.

Porosity of the active layer surface also was observed using SEM. Figure 2 shows morphology of the surface with almost uniform porosity. The crystalline structure of the composition after firing also can be observed from Figure 3. Three areas from the surface were chosen and the composition of the powders in these areas was analyzed using energy dispersive X-ray spectroscopy (EDX). A uniform distribution of the doping can be observed from Figure 4b.

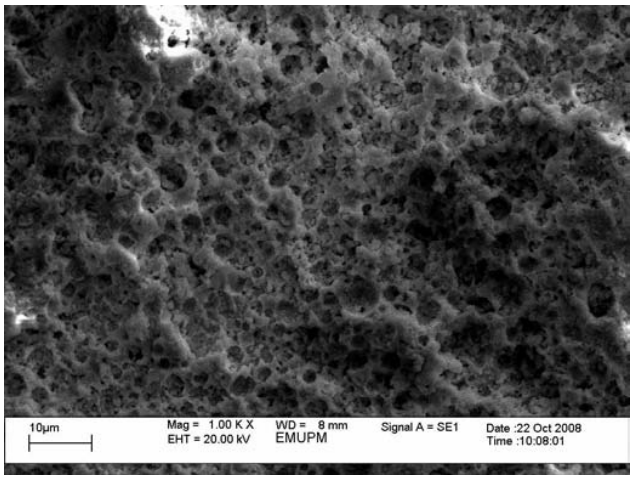


Figure 2: SEM result shows the porosity of sensor surface

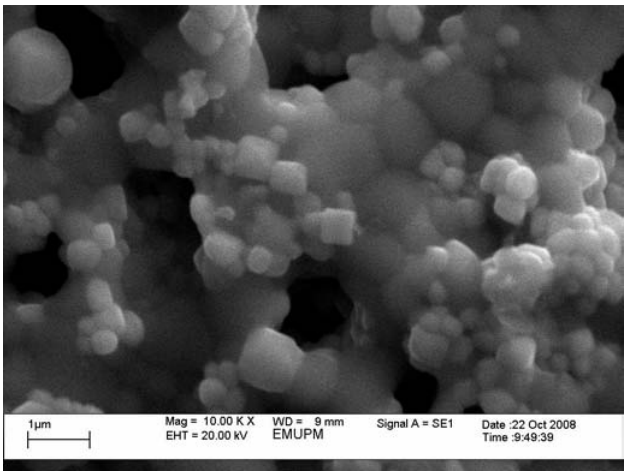
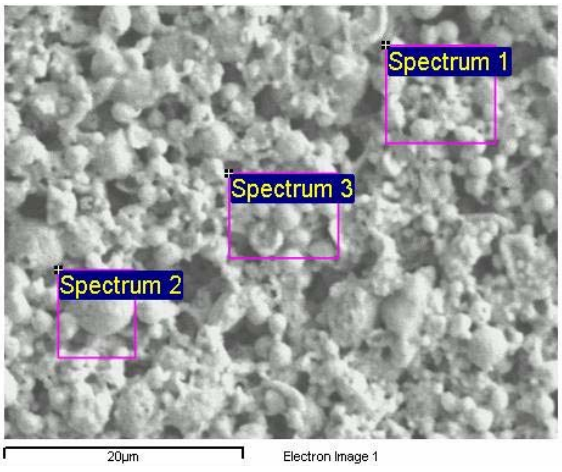
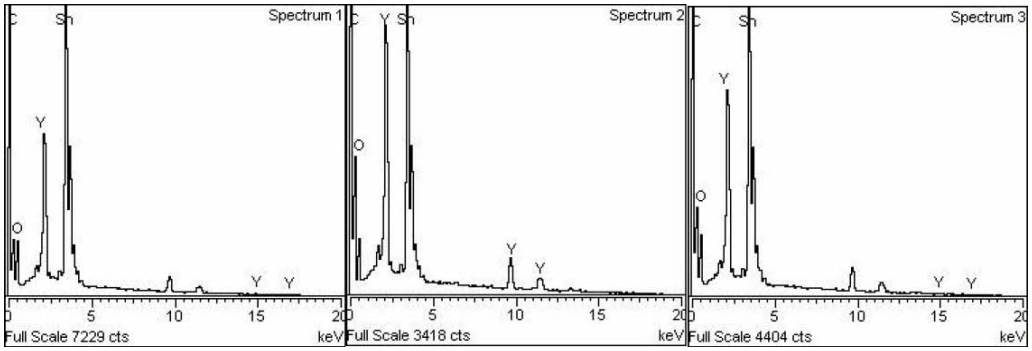


Figure 3: SEM result of crystallized surface



(a)



(b)

Figure 4: EDX analysis of surface of active layer (a) chosen areas (b) related spectrums

Electrical Properties

Different voltages were applied to the heater of sensors and the resistance across the electrodes was measured (Figure 5). The resistivity of the films decreases due to increasing of the heater temperature. The results show a higher resistance of the films doped with 15% yttria. Sensors then were exposed to the LPG as target gases and their response were recorded. At temperatures above 300 °C samples doped with 15% yttria also show a magnificent changing in resistance. Figure 6a and 6b show the measured resistance across electrodes in present of 250ppm and 500ppm LPG. Figure 7 shows the response of the samples in present of different volume of LPG at relative humidity of 45% and ambient temperature set at 27 °C. Heater temperature was set at 450 °C.

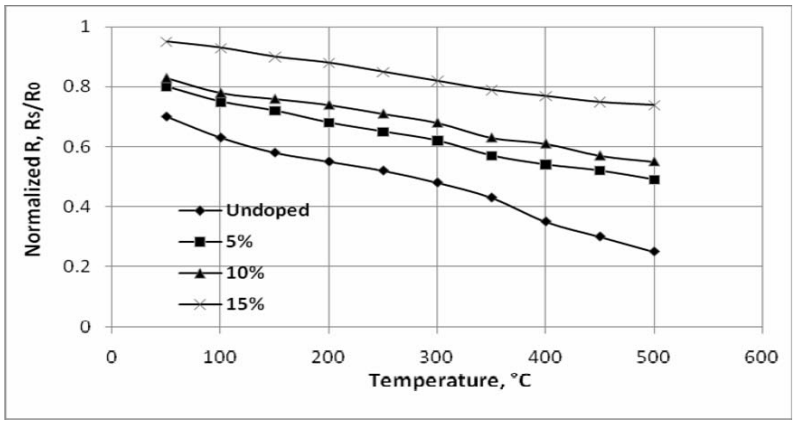
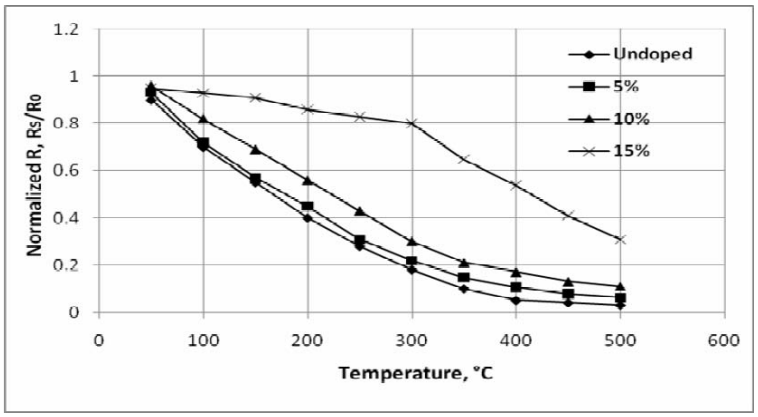
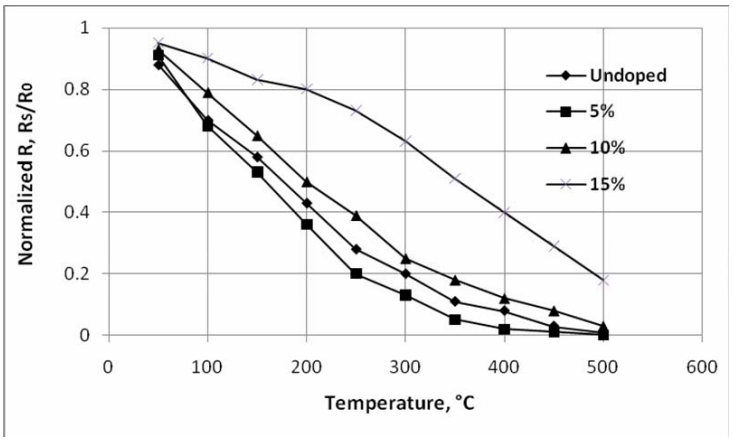


Figure 5: Normalized resistance across the electrode vs. heater temperature at fresh air.



(a)



(b)

Figure 6: Normalized resistance across the electrode vs. heater temperature in present of (a) 250ppm LPG (b) 500ppm LPG

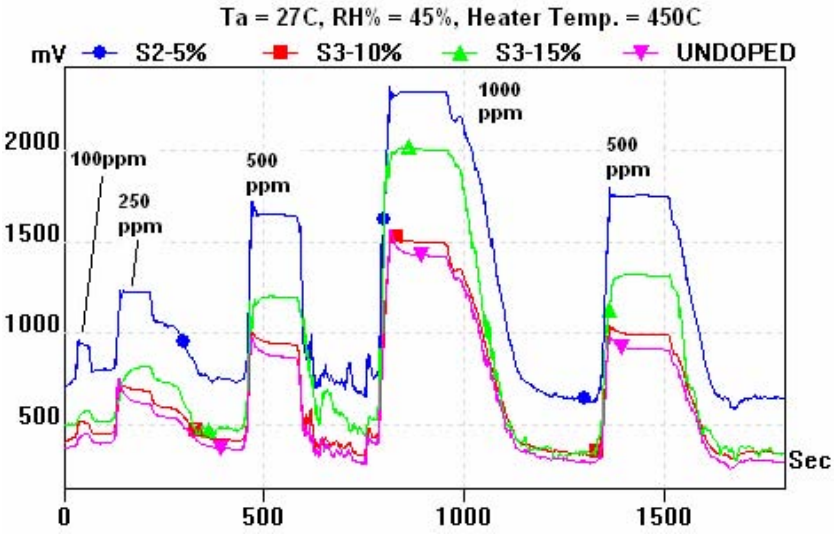


Figure 7: Response of samples to LPG

CONCLUSION

Response of pure SnO2 compared with different ratio of doped yttria in present of LPG. The results are shown a sensitivity of 5wt%Y2O3 doped into SnO2 to LPG started at 65°C and increased highly due to increasing of the heater temperature. Higher ratio of yttria causes lower sensitivity at lower temperature. Meanwhile increasing temperature of heater causes higher sensitivity but causes a magnificent increasing of power consumption of the sensor.

ACKNOWLEDGEMENT
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