GAS SENSOR BASED ON TIN DIOXIDE–CARBON NANOTUBES NANOCOMPOSITE FILM FOR ISOBUTANE DETECTION

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Abstract

Semiconductive gas sensors based on tin dioxide-multiwalled carbon nanotubes (MWCNTs) nanocomposite film for isobutane detection in atmosphere are presented and discussed in this paper. Gas sensor design, construction and characterization are described. Combination of LTCC technology and thick-film technology was chosen for construction of heater which is placed into a TO 8 package. This solution ensures reaching the high operating temperatures needed to achieve the best sensitivity. Three types of differently MWCNTs loaded SnO_2 based nanocomposite active films were deposited using spray-coating on a silicon substrate with an interdigitated structure. The first type was prepared from pure tin dioxide nanopowder only. Next two types of active layers were prepared as nanocompositions of tin dioxide nanopowder loaded with multiwalled carbon nanotubes (1.5 wt% and 3.0 wt%). All electrodes were tested in the gas chamber with changing concentration of isobutane in synthetic air. According to the obtained results it was found that the active layer with 3.0 wt% of multiwalled carbon nanotubes has the best sensitivity, response time and recovery time.

Keywords:

Tin dioxide, Carbon nanotubes, Nanopowder, Gas sensor, Isobutane

1. INTRODUCTION

Nowadays number of places with possible presence of dangerous gasses are increasing [1]. One of these gasses is isobutane, which in the air is extremely flammable even in very low concentrations (from 1.8 to 8.4 volume percent). It is very important to detect low concentrations in hundreds of ppm of isobutane in the air to avoid the risk of ignition. Resistive semiconductive gas sensor with active layer consisting of tin dioxide and MWCNTs has been already presented [2]. Main advantage of this active layer is low price and high sensitivity. This type of sensor has to be heated up to 450 °C because it is based on principle of chemisorption. Chemisorption is chemical binding between surface of active layer and anions from the air which needs certain activation energy [3]. Therefore it is very important to use materials which allow using of gas sensor in high temperatures. To reach the maximum reliability of heating element the LTCC technology with cermet thick-film pastes and kovar package can be used. The silicon substrate for active layer with gold/titanium interdigitated structure is good solution to improve sensitivity.

2. EXPERIMENTAL

a. Heating element

The first important part of metal oxide semiconductor gas sensor is the heating element. It has to allow to set heating temperature very precisely. Heater was designed and fabricated using a combination of the LTCC technology and thick-film technology on kovar package (see Fig 1). This solution allows heating up to

550 °C. Heating temperature is dependent on AgPd thick-film paste which bonds LTCC frame with TO-8 kovar package.

Fig. 1 LTCC frame (left) / heater (middle) and its placement in the TO-8 package (right)

The LTCC frame is laminated from four LTCC tapes HeraLock 2000 (Heraeus) according to the proposed design (see Fig. 2). Inner size of the frame is 8.5 mm × 8.5 mm which allows to insert the substrate with maximal dimensions of 8 mm × 8 mm.

The first LTCC layer includes the heating element fabricated from platinum thick-film paste ESL 5545-G (ElectroScience Laboratories) on the bottom side. On the top side of this layer are pads realized from gold LTCC paste TC8101 (Heraeus) for active layer connection. The second layer improves mechanical strength and two upper layers creating frame for fixing the substrate with active layer into the LTCC frame. Silicon substrate with active layer is glued by thick film paste FX 11-036 (Ferro). Melting point of glass component of this paste is 450 °C which is limiting for maximum heating temperature.

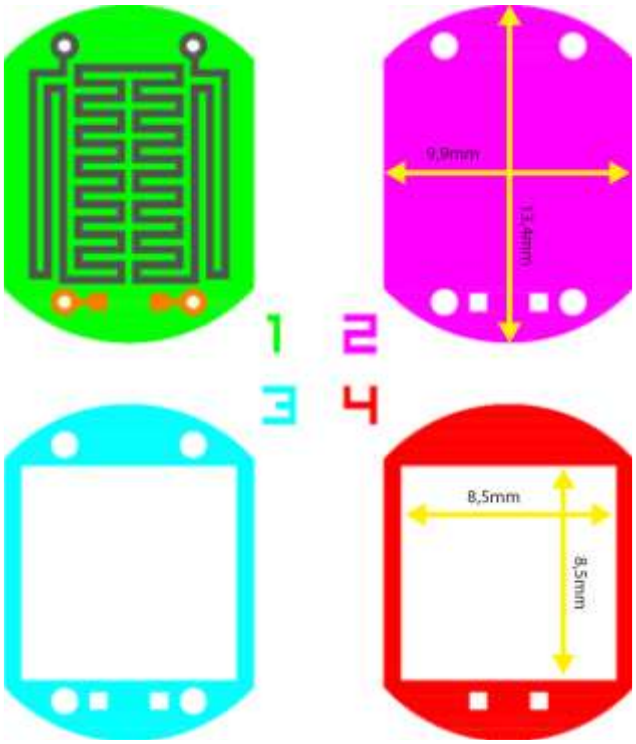

Fig. 2 Design of the LTCC heating frame

Heater has linear curve and allows to set temperature very precisely. Maximal consumption is 4.15 W at the maximum temperature of 450 °C.

b. Substrate with interdigitated structure for sensitive layer

The silicon wafer cut to 8 mm × 8 mm small pieces with interdigitated structure (see Fig. 3) was used as the substrate for active layer. Gap between combs was designed to be 50 µm and the width of comb was 100 µm. Sputtered titanium layer with thickness of 100 nm and gold layer with thickness of 250 nm were used for the fabrication of interdigitated structure. Titanium layer is used as adhesive layer for gold electrodes. It has good thermal stability which is sufficient for temperatures up to 450 °C. Gold layer on the titanium layer improves electrical conductivity and it is wire-bondable. The thermosonic wirebonding is necessary to provide electrical connection to LTCC frame.

Fig. 3 Interdigitated structure: design (left), its detail (middle) and fabricated sample (right)

c. Preparation and coating of sensitive layer

Three types of active layers were fabricated (see Fig. 4). The first one is unmodified and it was prepared only from pure tin dioxide nanopowder obtained from Sigma-Aldrich. The two others are modified with multiwalled carbon nanotubes – 1.5 wt% and 3.0 wt% respectively. These layers were spray-coated onto the silicon substrate with previously prepared interdigitated structure preheated to 170 °C. 1 ml of nanopowder dispersed in dimethylformamide was used for deposition.

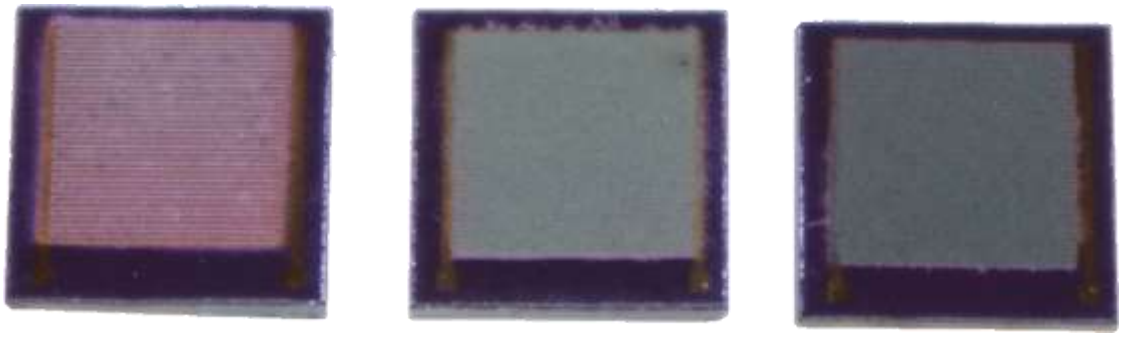

Fig. 4 Spray-coated active layers (from left: pure SnO_2; 1.5 wt% MWCNTs and 3.0 wt% MWCNTs)

The spray-coating was followed by annealing at 450 °C in vacuum chamber for 48 hours. The second step of annealing was made in flow gas chamber at 350 °C for 4 hours under the total flow of 500 sccm/min of 2500 ppm isobutane in synthetic air (both from Linde Gas, Czech Republic).

d. Measurement conditions

Sensors characterization was performed in the gas flow station (see Fig. 5) at constant pressure 1000 kPa and constant total flow 500 sccm/min. Temperature of flowing gas was in range from 23 °C to 28 °C. Each sensor was heated for 1 hour in synthetic air for its resistivity stabilization before starting of measurement. The concentration was changed from 50 ppm to 4000 ppm during the measurement process.

Fig. 5 Gas flow station for sensors characterization

3. RESULTS AND DISCUSSION

a. Influence of active layer composition on response

The first step of characterization was to find out which type of active layer has the best sensitivity for isobutane detection. Seven concentrations of isobutane (50, 100, 300, 500, 1000, 2000 and 4000 ppm) in synthetic air were measured. All three types of active layers were heated up to 350 °C during this characterization. This temperature was determined in previous experiments to be appropriate for obtaining the best sensitivity [4]. Calibration curves obtained from measurements are shown in the Fig. 6.

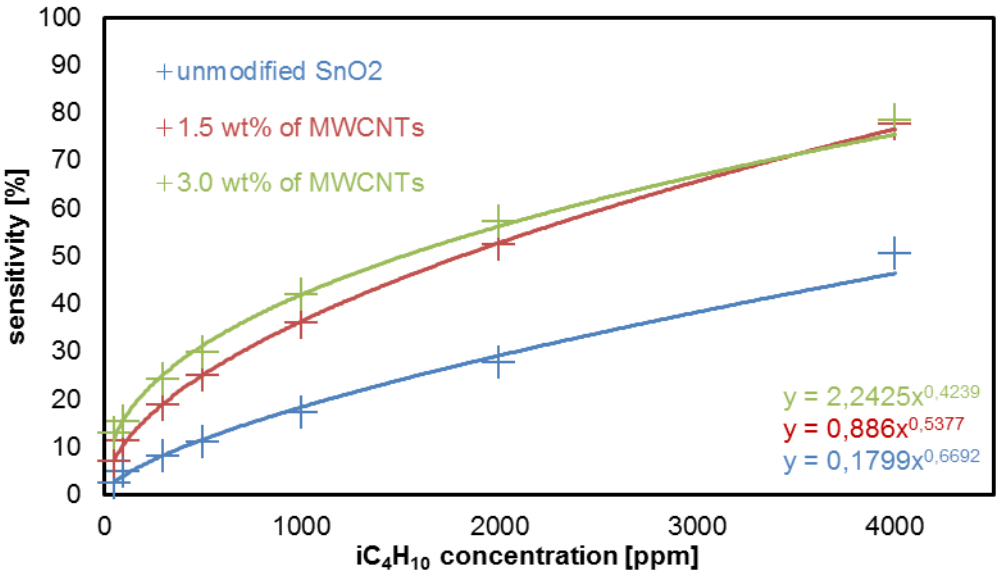

Fig. 6 Calibration curves of all three types of active layers

b. Influence of active layer thickness on response

From the previous subsection is clear, that the most loaded active layer with 3.0 wt% MWCNTs exhibited the best sensitivity. Therefore it was used for next experiments, where the appropriate active layer thickness was investigated. There were prepared four samples with different thickness (5.1 µm, 14.8 µm, 24.9 µm and 30.1 µm). The obtained results are shown in the Fig. 7. It was found that ideal active layer thickness for our requirements was 5.1 µm. The most linear curve and the most precise distinguishing of similar concentrations were achieved. From the Fig. 8 it is clearly visible that active layer with this thickness has very quick time constant (10.9 – 12.7 s) and quick time of recovery (20.1 – 21.5 s) which are necessary for good function of each sensor.

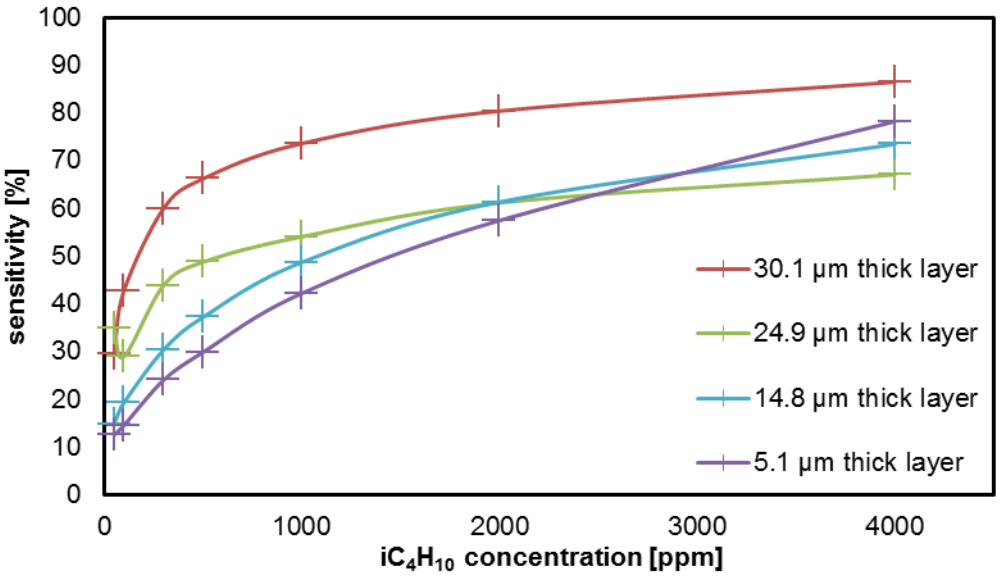

Fig. 7 Sensitivity of SnO_2/MWCNTs(3.0) active layers with different thicknesses

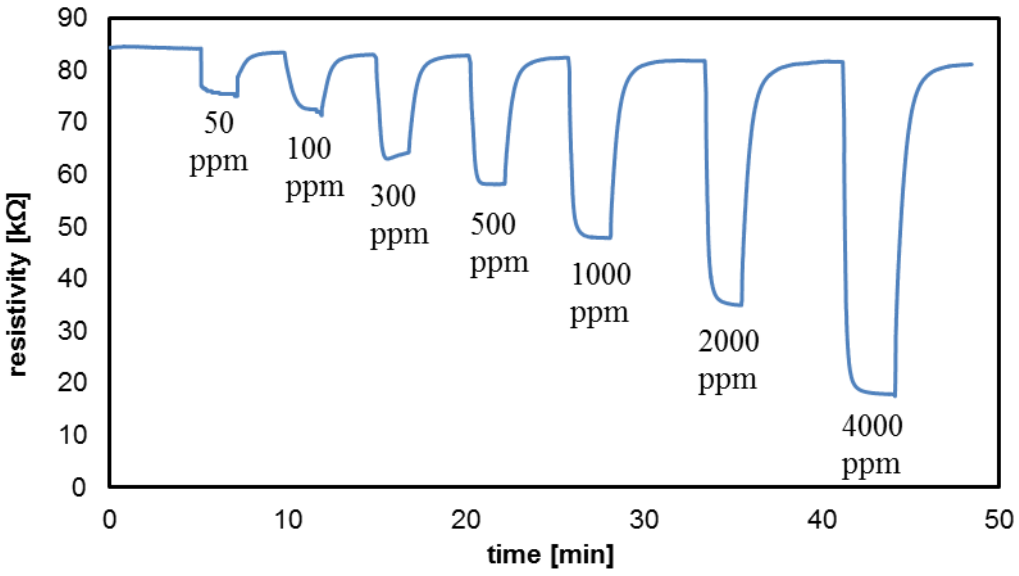

Fig. 8 Response of 5.1 µm thick SnO_2/MWCNTs(3.0) active layer to all measured isobutane concentrations

From the above mentioned results it is clear, that the SnO_2/MWCNTs(3.0) gas sensor (see Figure 9) has the best properties. 5.1 μm thick active layer was the best for our requirements due to its almost linear curve, quick response time and recovery time. It was able to detect 50 ppm of isobutane in synthetic air in 12.5 s with the 12.44% resistivity change. These values are excellent because of the risk of ignition of isobutane in the air is from 18 000 ppm to 84 000 ppm.

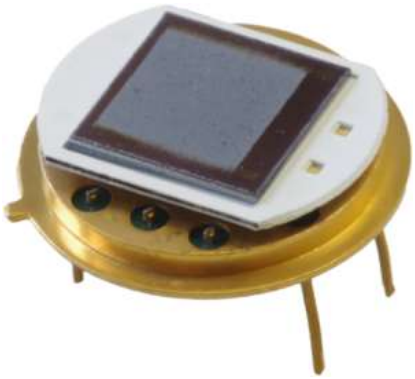

Fig. 9 Assembled SnO_2/MWCNTs(3.0) gas sensor

4. CONCLUSIONS

In this paper the tin dioxide sensor modified with multiwalled carbon nanotubes from its design to characterization is described. This sensor construction is very universal and is useable for many different active layers types with requirements for heating up to 450 °C. Our SnO_2/MWCNTs(3.0) sensor has very good properties and can be applicable in danger places where the isobutane or other organic gases can be detected. Its construction is very resistant to the environmental effects as is humidity or daylight for example.

5. ACKNOWLEDGEMENT

This work has been performed in laboratories supported by the operational program Research and Development for Innovation, by the SIX project CZ.1.05/2.1.00/03.0072 and supported by Grant Agency of the Czech Republic under the contract GACR P205/10/1374.

6. REFERENCES

[1] YAMAZOE, N., et al. Enviromental gas sensing, *Sensors and actuators B*, 1994, 20, p. 95-102.

[2] AROUTIOUNIAN, V.M., et al. Manufacture and investigation of gas sensor made of CNT/SnO_2 tube, Armenian Journal of Physics, 2011, 4, p. 206-210.

[3] BARSAN, N., et. al. Fundamental of Metal Oxide Gas Sensors, *The 14th International Meeting on Chemical Sensors*, 2012, p. 618-621.

[4] GABLECH, I. Tin dioxide based semiconducting gas sensors, *Master´s thesis,* 2014, 49.