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Fabien Le Pennec, Sandrine Bernardini, Mohamad Hijazi, Carine Perrin-Pellegrino, Khalifa Aguir, et al.. Screen Printed BaTiO 3 for CO 2 Gas Sensor. The Fifth International Conference on Advances in Sensors, Actuators, Metering and Sensing, Nov 2020, Valencia, Spain. hal-02529671

HAL Id: hal-02529671

https://hal.science/hal-02529671

Submitted on 2 Apr 2020

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Screen Printed BaTiO₃ for CO₂ Gas Sensor

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Abstract—In this work, we report on a new evaluation of metal oxide based on carbon dioxide sensors, using barium titanate nano-powder. The sensing principle is based on a change in conductance of semiconducting oxides when carbon dioxide is present. The sensitive layer was deposited on a SiO_2/Si substrate by screen printing technology. The sensor responses were studied between 100 and 5000 ppm of carbon dioxide in the air with 50% relative humidity. The sensor presents good sensitivity toward carbon dioxide, with a stable baseline, and fast response and recovery time. These results are promising for carbon dioxide sensing.

Keywords-Gas Sensor; CO₂; BaTiO₃; Metal Oxide; Environment.

I. INTRODUCTION

Carbon dioxide (CO₂) is one of the main gases responsible for the greenhouse effect and, consequently, the global warming trends. Hence, its monitoring is subject of a major societal challenge. With an outdoors concentration up to 500 ppm in urban areas, the ventilation balance is affected and the development of reliable low-cost CO₂ sensors at multiple sites becomes an industrial strategy. Nowadays, the most commonly used method to detect CO₂ is based on optical sensors. Despite their efficiency in CO₂ detection, these technologies are expensive, have high electric consumption and are not fully miniaturized. Metal oxide gas sensors show potential features such as low-cost, mass production, miniaturization, fast response and recovery times.

In 1991, Ishihara et al. [1] first proposed a composite material based on p and n-type semiconductors, by mixing copper oxide (CuO) and barium titanate (BaTiO₃) powders. In 2001, Liao et al. [2] showed that pure CuO and pure BaTiO₃ gave no response to CO₂. Since then, these pure materials have been definitively abandoned and only composites have been studied. But, the sensors of Liao et al. [2] were in the very basic form of large discs of sintered powders with unknown granularity, connected by Ag paste electrodes. Thus, we propose herein a new evaluation of BaTiO₃ based CO₂ sensors.

The rest of the paper is structured as follows. In Section II, we describe our approach based on BaTiO₃ nano-powder deposition on platinum interdigitated electrodes by screen printing, a low cost, and an easily used technique. Then, in Section III, the sensing results are discussed based on a change in conductance of BaTiO₃ when CO₂ are introduced.

Finally, a conclusion is given in Section IV.

I. DESCRIPTION OF APPROACH AND TECHNIQUES

This description is composed of two parts; one is the sensing film fabrication; the other is the measurement system set-up.

A. Gas sensors

Our gas sensor is made of Ti/Pt interdigitated electrodes (5 and 100 nm, respectively) deposited on Si/SiO₂ by magnetron sputtering. BaTiO₃ thick films were deposited by screen printing on these electrodes to produce a CO_2 sensitive layer. BaTiO₃ nano-powder (<100 nm, 4 g) was mixed with glycerol (1.5 g) and screen printed on Si/SiO₂ substrate with interdigitated platinum electrodes spaced by $50 \mu m$ (Figure 1).

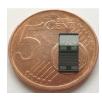


Figure 1. Sample image of SiO₂/Si substrate (4 x 4 mm²) with platinum electrodes (bottom) and the final sensor with the BaTiO₃ thick film (top).

The deposited film was annealed at 400°C on a hotplate, in ambient air. The film structure was determined by X-Ray Diffraction (XRD) with a Philip's X'Pert MPD equipment $(\lambda = 1.54 \text{ Å})$.

B. Setup

0.1 V DC voltage was applied to the sample while the electrical resistance was monitored by a homemade LabVIEW program using a Keithley Model 2450 Source Measure Unit (SMU) Instrument (Keithley, U.S.A.). Dry air (no humidity) was used as both the reference and the carrier gas. A gas dilution and humidification system generates an output mixture at the target CO₂ concentrations (1 to 5000 ppm) with a variable humidity (0% to 90%). The sensing properties of BaTiO₃ sensors were tested by measuring the sensor resistance for 5 min under CO₂ diluted in dry air and in humid air with a standard Relative Humidity (RH) value of 50 %. The sensors were operated at several temperatures from 200°C to 300°C on a hotplate. A constant total flow was maintained at 500 Standard Cubic Centimeters per Minute (SCCM) via mass flow controllers.

III. RESULTS AND DISCUSSIONS

The XRD diffractogram of BaTiO₃ thick film (Figure 2) shows the presence of BaTiO₃ nanocrystals in the tetragonal phase of BaTiO₃ [3].

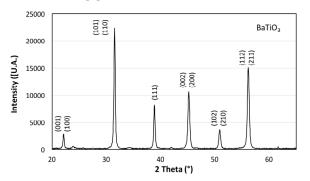


Figure 2. BaTiO₃ diffractogram using $\lambda = 1.54$ Å (Philip's X'Pert MRD).

The BaTiO₃ sensors for different CO₂ concentrations provide a measurable response depending on the CO₂ concentrations in the 100 - 5 000 ppm range and 50% RH at various temperatures. The higher response amplitude variations were obtained at 280°C. Figures 3 and 4 show, respectively, the response and the sensitivity of the BaTiO₃ sensor under CO₂ in the air with 50% RH at 280 °C, the optimum working temperature. It gives reversible responses to CO₂ concentrations between 100 ppm and 5000 ppm.

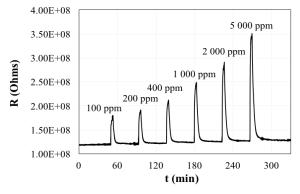


Figure 3. Resistive responses of $BaTiO_3$ to six CO_2 concentrations with 50% RH at $280^{\circ}C$.

The sensor response is defined in (1) as the ratio between the sensor resistance under CO_2 exposure and the sensor resistance in the air:

$$R = R_{gas} / R_{air}$$
 (1)

where R_{air} is the sensor resistance through humid airflow and R_{gas} the sensor resistance in the presence of CO_2 .

The response time was less than 2 minutes and the recovery time was about 5 minutes. The responses are proportional to the CO_2 concentrations, and they restored the original baseline in less than 5 minutes.

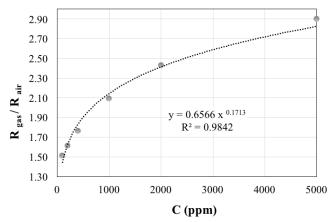


Figure 4. Sensitivity response of $BaTiO_3$ to different concentrations of CO_2 with 50% RH at 280 $^{\circ}C.$

These results are in agreement with the recent review on chemiresistive CO_2 gas sensors [4].

IV. CONCLUSIONS

This work reported preliminary results on a screen printing BaTiO₃ sensor working at an optimum temperature of 280°C and for 50% RH. Our experiments showed stable baseline responses with fast response/recovery times towards CO₂. These sensors seem promising for measuring indoor and outdoor air quality and for CO₂ detection. However, after a few weeks, using the same operational conditions, the sensor responses were weakened on the record. New experiments and analyses are in progress to understand this phenomenon.

ACKNOWLEDGMENT

The authors thank Mr. A. Combes and Dr. T. Fiorido for their technical support.

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