

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 SiO₂/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.

II. 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 CO₂ 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 μm (Figure 1).

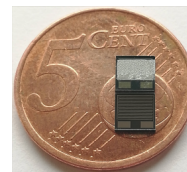


Figure 1. Sample image of SiO₂/Si substrate (4 x 4 mm²) with platinum electrodes (bottom) and the final sensor with the BaTiO₃ thick film (top).

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 ($\lambda = 1.54 \text{ \AA}$).

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].

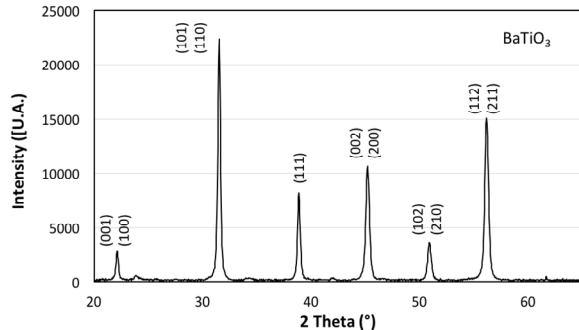


Figure 2. BaTiO₃ diffractogram using $\lambda = 1.54\text{\AA}$ (Philip's X'Pert MRD).

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.

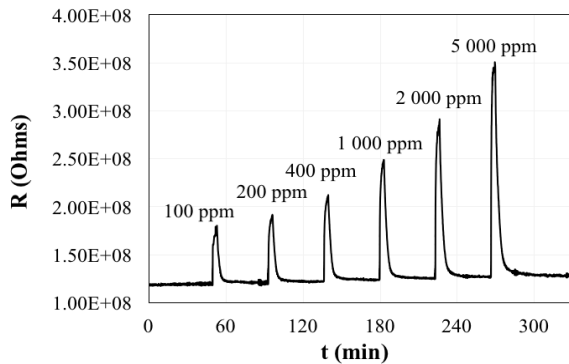


Figure 3. Resistive responses of BaTiO₃ to six CO₂ concentrations with 50% RH at 280°C.

The sensor response is defined in (1) as the ratio between the sensor resistance under CO₂ exposure and the sensor resistance in the air:

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

where R_{air} is the sensor resistance through humid airflow and R_{gas} the sensor resistance in the presence of CO₂.

The response time was less than 2 minutes and the recovery time was about 5 minutes. The responses are proportional to the CO₂ concentrations, and they restored the original baseline in less than 5 minutes.

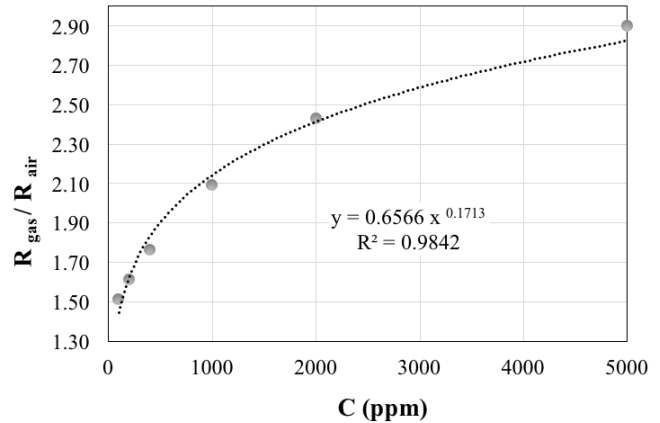


Figure 4. Sensitivity response of BaTiO₃ to different concentrations of CO₂ with 50% RH at 280°C.

These results are in agreement with the recent review on chemiresistive CO₂ 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.

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