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Influence of Lanthanum Oxycarbonate Deposition on Carbon Dioxide Detection

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Abstract—Lanthanum oxycarbonate films have been deposited by drop coating and screen printing for carbon dioxide detection. The measurements are based on a change in resistance and provide sensitive responses to carbon dioxide concentrations in a humid environment. Electrical measurements were made at 5 000 ppm of carbon dioxide in synthetic air. The relative humidity was maintained at 50%. Our results highlighted the close link between the morphology of the sensitive elements and the electrical responses of the sensors, and thus the need to master the deposition technique.

Keywords—Gas sensor; CO_2 ; La_2O_3 ; Rare earth oxide; Environment.

I. INTRODUCTION

Indoor air quality (IAQ) is a major issue because of the high mortality rates caused by indoor pollution. The World Health Organization (WHO) estimated that more than 4 million people died in 2020, and this trend is expected to increase in the coming years. In this context, several studies show that the analysis of the amount of carbon dioxide (CO_2) in a confined space is a good indication of air containment [1]. Air quality monitoring based on CO_2 detection can be a good solution for public buildings or industrial sites [2]. Moreover, with the recent appearance of the health crisis (Covid-19) affecting all the countries, the concept of indoor air quality is increasingly emphasized [3,4]. The probability of virus transmission increases when a room is poorly ventilated. Thus, measuring the CO_2 level in a confined space could help verify that the air is sufficiently renewed and thus help minimize the transmission of Covid-19. However, current CO_2 detection techniques using infrared sensors are expensive despite their high sensitivity. This is why many research teams are working on semiconductor materials (metal oxide, rare earth oxide, ...) for the many advantages they can offer, such as: low cost manufacturing of sensors and high miniaturization. Several materials used are referenced in the literature as $\text{La}_2\text{O}_3\text{-SnO}_2$ [5], CaO-ZnO [6], BaTiO_3 [7], $\text{CuO-BaTiO}_3\text{@Ag}$ [8], and $\text{La}_2\text{O}_2\text{CO}_3$ [9]. They present a good sensitivity to a CO_2 exposure. The last material, La oxycarbonate shows a high sensitivity to CO_2 . Various studies have been carried out on this type of material, such as the performance investigation under CO_2 [10], the synthesis process on morphology [10, 11] or the kinetics of carbonation and decarbonation between $\text{La}_2\text{O}_3\text{-La}_2\text{O}_2\text{CO}_3$ under CO_2 [13]. Other authors such as Kodu et al. [14] and Suzuki et al. [15] have studied this chemoresistive material for the CO_2 sensing. The first author demonstrated the importance of the annealing film on crystalline type oxycarbonate films. Other researcher team focused on the reaction mechanism between $\text{La}_2\text{O}_2\text{CO}_3$ and the absorbents. For both teams, they have got high sensitivity for a CO_2 exposure but they have measured a

high resistance that is not suitable for a microsensor device. Considering that the sensor resistance is dominated by a double Schottky barrier at the grain boundaries [15], we have compared the CO_2 detection of lanthanum layers deposited by two techniques: drop coating and screen printing. In the presence of 50% humidity, the detection performance was studied as a function of operating temperatures for a concentration of 5000 ppm CO_2 . Our detection results demonstrated the influence of the carbonate lanthanum morphology induced by the deposited method.

II. EXPERIMENTAL

This section is devoted to the description of the sensor fabrication and the electrical set-up.

A. CO_2 sensor fabrication

The CO_2 sensors were realized by drop coating and screen-printing methods (Fig.1). The solution used for the drop coating was obtained by mixing 0.3g of La_2O_3 nano-powder (<100 nm, Sigma-Aldrich®) in 10mL of ethanol and 2 mL of glycerol. The solution was dropped with a glass Pasteur pipette on Si/SiO₂ transducer with Ti/Pt interdigitated electrodes (180 nm height). To prepare the sensitive material paste for the screen-printing method, 0.3g of the same La_2O_3 nano-powder was mixed with 1 mL of glycerol and mashed with a mortar/pestle. The La_2O_3 paste was spread out through screen mesh and deposited on the same transducer used by drop coating. For both methods, we dried the solvents with a hot plate at ambient air. The sensors were dried at 70°C for 10 min or/and then at 130°C for 10 min to remove ethanol and glycerol, respectively, depending on the deposited method used. To ensure solvent removal and oxycarbonate formation, a high temperature (450°C) for 3 min on the hot plate in ambient air was applied.

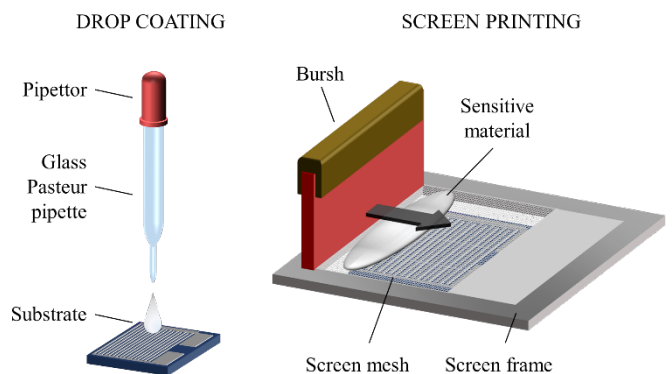


Fig. 1. Schema of our deposition process : drop coating and screen printing of $\text{La}_2\text{O}_2\text{CO}_3$ on a Si/SiO₂ substrate (4 x 4 mm²) with Pt/Ti interdigitated electrodes.

The film structures were determined by X-Ray Diffraction (XRD) with a Philip's X'Pert MPD equipment ($\lambda = 1.54 \text{ \AA}$). The acquisition was performed between 20° and 70° with $0.02^\circ/\text{step}$. Morphological images were acquired using a Zeiss GeminiSEM 500 ultra high-resolution Field Emission Scanning Electron Microscope (FESEM).

B. Electrical set-up

The electrical characterization consists of a three-part test bench, including a gas and a humidity generation system, a thermostatically chamber to control the external environment of the test chamber, and a data acquisition system. Detailed information on the acquisition system is described in a previous study [16]. This equipment allows to control the dilution of CO_2 in a neutral carrier gas flow (air). Electrical acquisition under wet conditions is required and operated by a steam injection device (Fig. 2). The arrangement of mass flow controllers (MFC) allows the dilution of the gas concentration and the moisture content to be precisely controlled between 0 and 80%.

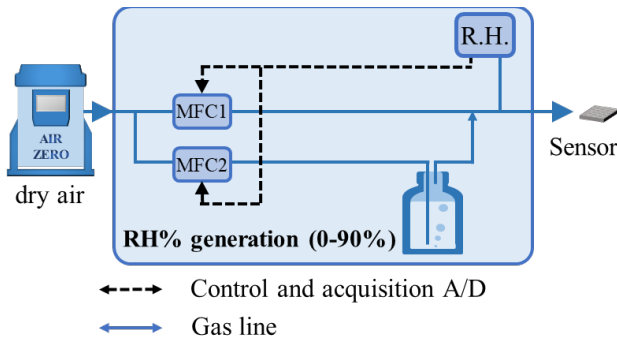


Fig. 2. Test bench schema presentation.

We applied a constant voltage of 1V and a gas flow of 500 Standard Cubic Centimeters per Minute (SCCM) to study the sensing properties. For both deposition methods, the operating temperature was controlled in a temperature range of 200°C to 300°C . We generate 5 000 ppm of CO_2 by the mixture of synthetic air and CO_2 diluted in humid air to test the sensor responses.

The best compromise in sensor performance for this work was obtained at 290°C . The sensor response is defined in (1):

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

where R_{gas} is the sensor resistance under CO_2 exposure and R_{air} is the sensor resistance in air.

III. RESULTS AND DISCUSSION

This section is composed of two parts: one section is devoted to the comparison of the sensing film morphology, while the other is devoted to the discussion of the electrical results.

A. Chemical and Structural characterisation

For the structure analysis, the sensitive material on a Si/SiO₂ substrate was deposited by the both methods. The X-ray diffractograms of $\text{La}_2\text{O}_2\text{CO}_3$ films show the presence of crystalline layers with monoclinic phase $\text{La}_2\text{O}_2\text{CO}_3$ (Fig. 3)

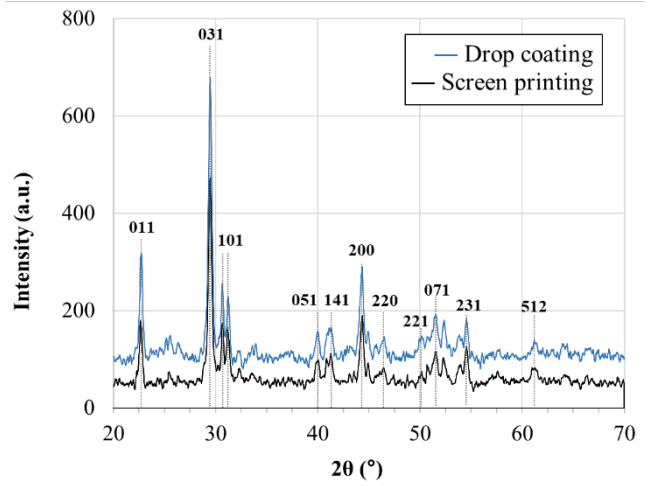


Fig.3. Diffractogram of the sensitive layer deposited by drop coating and screen printing on a Si/SiO₂ substrate ($4 \times 4 \text{ mm}^2$) with Pt/Ti electrodes layer on using $\lambda = 1.54\text{\AA}$ (PANalytical EMPYREAN).

according to the JCPDS: 48-1113 for both methods. Our diffractograms are in agreements with the diffractogram previously obtained by Bakiz *et al.* [13].

Oxycarbonate formation was obtained from the La_2O_3 nano-powder and flash dried at high temperature in ambient air. The $\text{La}_2\text{O}_2\text{CO}_3$ films deposited by drop coating and screen printing were characterized by scanning electron microscopy as shown in Fig.4. The pictures clearly illustrate the different morphologies.

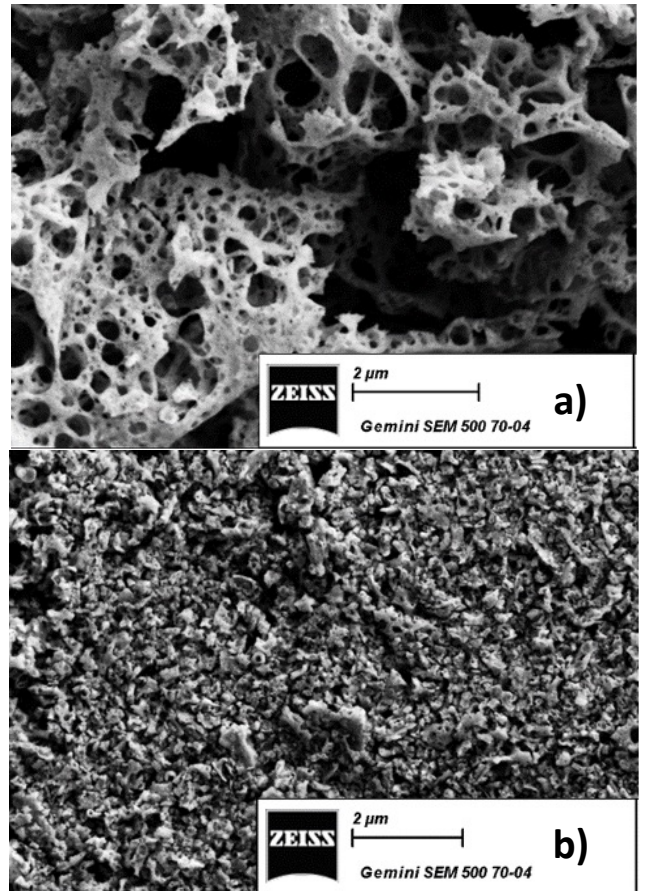
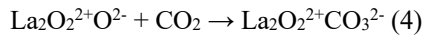
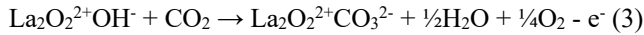
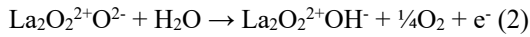
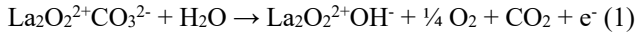


Fig. 4. SEM images of $\text{La}_2\text{O}_2\text{CO}_3$ deposited by (a) drop coating and (b) screen printing.

The layer obtained by drop coating shows a high porosity at the microscopic scale compared to screen printing. This difference can be explained by the mash stage introduce to mix the La₂O₃ nanopowder in the glycerol.

B. Electrical sensor study

As presented in Fig. 5, the drop deposited La₂O₂CO₃ films have high resistance and give no response under CO₂ and humid air at 290°C. At the same temperature, the screen-printing films were less resistive and gave a response to CO₂ ($R_{\text{gas}}/R_{\text{air}} = 13.8$). We note the need to work in a humid environment, without this, the resistance was too high and out of our acquisition limit. Furthermore, the resistance variation between the sensors fabricated by the two deposition methods can be explained by the morphology of the sensitive layer. Liu *et al.* [17] shown a strong dependence of the porosity on conductivity of the metallic material. This model can be applied to our observations on the resistance of rare-earth oxycarbonate. According to [15], the reaction model is explained by the La₂O₂²⁺ presence formed on the La₂O₂CO₃ surface which reacts with the adsorbates (CO₃²⁻, OH⁻, O²⁻). Thus, the CO₂ sensitivity with La₂O₂²⁺ forms is based on a competitive adsorption between carbonate and hydroxyl groups. The following reactions describe the different possibilities that can occur on the sensitive layer surface when exposed to CO₂ under humidity [15]:



The equations (1) and (2) describe the reaction causing a decrease in resistance and conversely the equations (3) and (4) induce an increase in resistance. Therefore, the presence of La₂O₂²⁺OH⁻ on the surface of the sensitive layer depends on the moisture conditions and induces a change in the resistance according to the reaction (3). The optimal temperature was evaluated and set at 290°C for the screen-printing method, because below this temperature, at 275°C, our test bench reaches its measuring limit as shown in fig. 6.

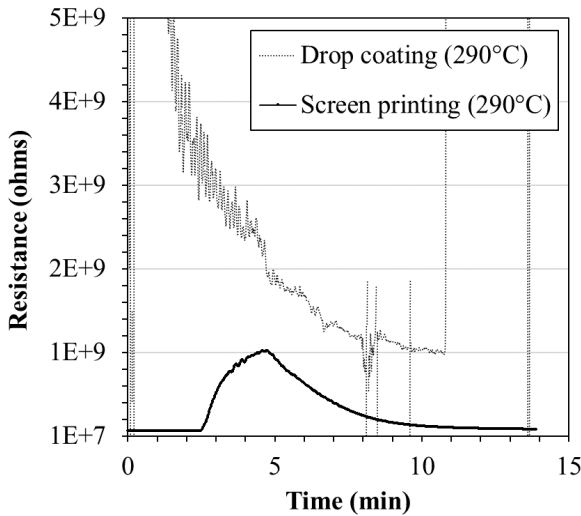


Fig. 5. Resistance variation to CO₂ exposure at 290°C in 50% humidity for La₂O₂CO₃ films obtained by drop coating and screen printing.

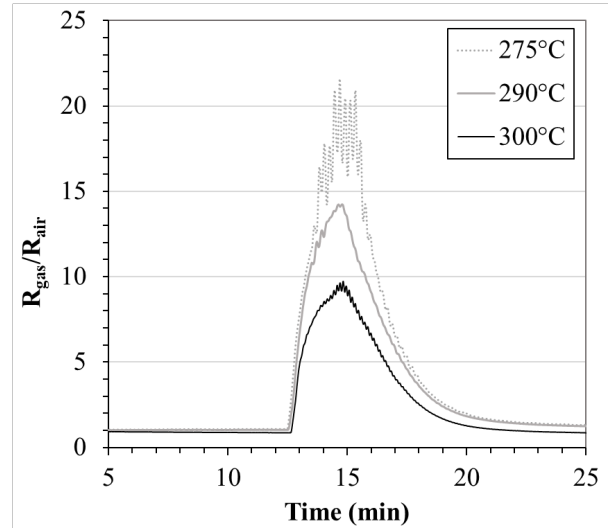


Fig. 6. Normalized responses for 5 000 ppm of CO₂ at 50%R.H for sensors fabricated by screen printe. (parameters: 1V/10μA/500 SCCM).

Above this temperature the sensitivity decreases with increasing temperature as shown in Fig. 6. That can be explained by the La₂O₂²⁺OH⁻ decrease with the temperature rise

CONCLUSION

We deposited La₂O₂CO₃ films by drop deposition and screen printing. Our results demonstrated the influence of morphology on the measured resistivity and the sensor response under exposure to CO₂ in humid air. Our measurements at 50% R.H. and 290°C, gave a normalized response equals to 13.8 for sensors fabricated by screen printing. The high porosity induced by the drop coating method did not allow us to measure a sufficiently low resistance and obtain a response to CO₂. This result can be explained by the sensor resistance which is dominated by a double Schottky barrier at the grain-grain boundaries [15] and the strong dependence of the resistance on the porosity structure. The operating temperature determination was limited by our acquisition system due to high resistance measured.

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