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MOX Resistive Microsensors for Low Concentration Methane Detection †

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Abstract: A series of MOX resistive sensors, having CuO and CoO sensitive films were prepared using an eco-friendly technique (sol-gel). The sensor transducers are based on a custom made alumina wafer, having gold (Au) or platinum (Pt) interdigital electrodes (IDE) printed onto the alumina surface. Sensor response (sensor electrical resistance variations, measured at the IDE's contact pads) was recorded under lab conditions (dried target and carrier gas from gas cylinders), in a constant gas flow and a 1.5 Volts direct current (DC) applied to the IDE- as sensor operating voltage.

Keywords: films; sol-gel; alumina wafer with Pt(Au) IDE; methane; lab conditions

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1. Introduction

Methane is a odorless and colorless gas with a major greenhouse effect. It can accumulate gradually, up to explosive concentrations (50,000 ppm or 5% volume), so its detection is very important for safety reasons. Human activities that emit methane include mining industry or LPG refining. Methane is also emitted from natural sources, such as natural wet areas (swamps). NIOSH (National Institute for Occupational Safety and Health's) established a maximum limit of 1000 ppm [1], for an exposure time of 8 hours, at the workplace. Detection of methane by humans without specialized equipment (sensors) is impossible, methane being as previously mentioned, odorless and colorless.

The most widely spread gas detectors are MOX based (contain a form of metal oxide as sensitive material in contact with electrodes). For MOX gas sensors, the principle of detection is based on the electrical *resistance change* which is caused by the surface reaction between the target gas and the metal oxide (acts as catalyst) deposited on the surface of the sensor (in this case called *chemiresistor*), upon sensor exposure to different gaseous atmospheres [2].

Although CuO and CoO, in different combinations, were previously used as sensitive materials for different gases (detection for VOC's, NH_3, carbon oxides, H_2S were summarized in ref. [2]), methane detection using these oxides was very rarely reported, and usually high-cost preparation techniques [3,4], high working temperature, or with incomplete sensor characterization [5] (e.g. influence of humidity, cross-response measurements) are reported.

In this paper we report preliminary results regarding methane detection, within NIOSH recommended limits, using abundant sensitive oxide materials (films of CuO and Co), obtained via an eco-friendly low cost technique (sol-gel), at low sensor operat-

ing temperatures, with fast response/recovery sensor characteristics.

2. Materials and Methods

Sensitive films were obtained using the sol-gel spinning method (1000 rotations/min). As precursors, the basic carbonates of the respective metals were used ($Cu(CO_3)_2Cu(OH)_2$ for CuO, and $Co(CO_3)Co(OH)_2$ for CoO).

The deposited films were stabilized by thermal treatment after the deposition stage.

Own-design alumina transducers were used, with the following dimensions: 5x10x0.6 mm. The transducers contained Pt or Au IDE's on one side, and a Pt heater on the opposite side of the transducer.

All sensor determinations were carried out under laboratory conditions, using dry, high purity gases. Sensor operating voltage was 1.5 V direct current (DC), the tested working temperatures (T_w) were in the range situated between room temperature and 220 °C (specific for each sensor used), and the sensing experiments were carried out in a continuous flow of gas (max. 180 mL/min). The target gas concentrations were achieved using a calibrated system of mass-flow controllers (MFC). The two separate gas flows are mixed inside a special glass vessel, shown in the scheme of the experimental installation (Figure 1), using an on-off valve system.

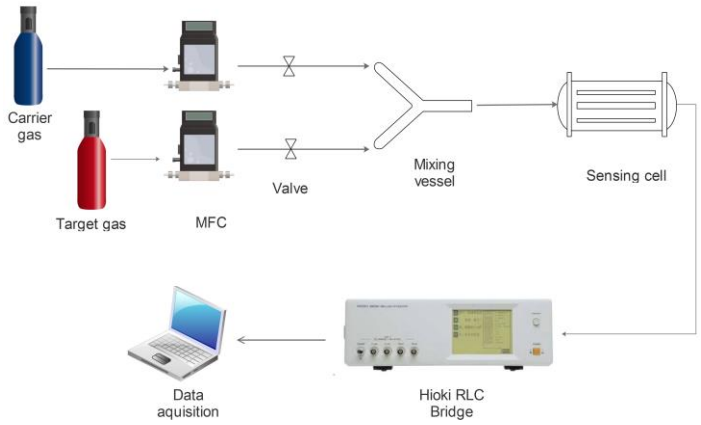

Figure 1. Schematic representation of the gas sensing experimental setup.

The mixed gases (carrier and target gas) are then inserted into an own-design sensor cell, which contains the investigated sensor. A chemical reaction takes place (between the sensitive oxide material and the target gas molecules) on the surface of the sensor, which leads to a change in its electrical resistance, a variation recorded by the RLC bridge connected to the sensing cell.

3. Results and Discussion

Gas Sensing Experiments

The following sensors were prepared (listed in Table 1):

Table 1. The investigated sensors and their composition.

Sensor Abbreviation *	Sensitive Film	Transducer (IDE/Wafer)
S3	CuO	Au/Al_2O_3
S4	CuO	Pt/Al_2O_3
S5	CoO	Pt/Al_2O_3

* As denoted during sensing experiments.

It can be observed that the sensors having CuO sensitive films are available with two IDE types, gold (Au) or platinum (Pt), to investigate the influence that the IDE material may have. Figure 2 evidences the response/recovery characteristics of the sensors presented in Table 1. S4 sensor has a slightly higher working temperature—T_w (220 °C, comparing with 210 °C for the other two sensors-S3 and S5). Sensor responses are comparable, when using different noble metals such as Pt or Au as IDE (S4, S3). Cobalt based sensor-S5 seems to be performing slightly better than the copper based sensors -S3, S4.

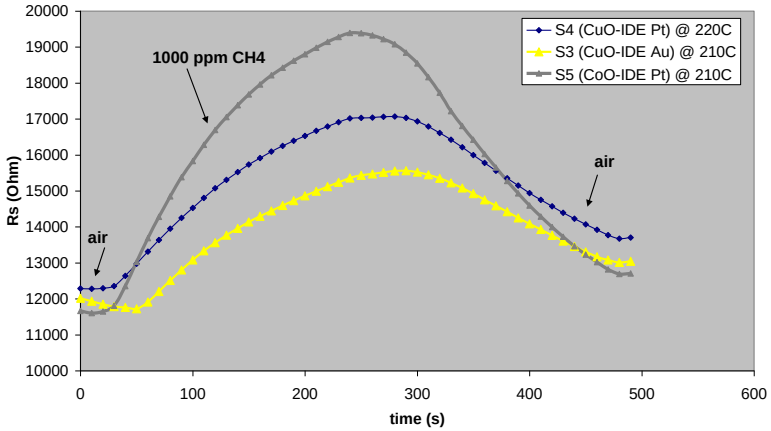

Figure 2. The response/recovery of the tested sensors, for 1000 ppm CH_4, at T_w specific to the investigated sensors (210–220 °C).

The response of the sensors is fast (250 s) and their recovery is complete (250 s), thus making it possible to resume the sensing experiments, after the corresponding recovery cycle, without sensor replacement. Further investigations regarding sensitive surface characterization, sensor sensitivity, selectivity and stability are currently undergoing, but based on the preliminary results obtained so far, we can state that the obtained sensors are promising candidates for the development of a new commercial methane detection sensor.

4. Conclusions

Sensors with CuO and CoO sensitive films have been prepared via an eco-friendly low-cost technique (sol-gel) and tested for methane detection. Preliminary test results showed that the obtained sensors have successfully detected methane, with a fast response (250 s) and a full recovery (250 s). The tested concentration of 1000 ppm CH_4 in air represents the NIOSH maximum allowed limit, for an exposure time of 8 h, at the workplace. Based on the reported preliminary results we can conclude that the obtained sensors are promising candidates for a new MOX-based methane detection resistive sensor (MOX chemiresistor).

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