SAW-based Differential Sensor Exploiting Metallocorroles Properties For The Selective Measurement Of Carbon Monoxide

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***Abstract*— During the last decades, the potential impact of indoor air quality on human health has stimulated an interest in hazardous compounds survey, such as carbon monoxide (CO). The detection of these compounds has consequently become a vital need. To address this issue, we propose a Surface Acoustic Wave (SAW) device functionalized with metallocorroles used for the selective detection of CO. Here, we insist on the necessity to detect CO in the presence of interferents, such as O_2 that is obviously present in the air, carbon dioxide (CO_2) present in significant quantity in urban area (400 ppm) and humidity (H_2O) which is a well-known interferent in the case of SAW-based gas sensors. Here, we report on the interest of a differential configuration of the sensor that takes advantage of accurate organic layers, to improve the stability of the sensor's signal and lower the sensitivity to interferents. As an introduction, we provide the context of this study and introduce the two main components of our sensor, which are the SAW device and the metallocorroles.**

Keywords- Gas sensor; Carbon monoxide; SAW; metallocorroles.

I. INTRODUCTION

Indoor air quality monitoring has become a subject of increasing importance since a few decades [1]. Among gases (such as CO, CO_2, NOx, etc) produced by combustion or delivered (such as formaldehyde, benzene, ethylene glycol) by furniture, detection of carbon monoxide is of great importance due to its characteristic: this colorless, tasteless and odorless gas is impossible to detect by human beings. Moreover, the LC_{Lo} is about 5 000 ppm in 5 minutes [2]. The French Institute for Health Surveillance (INVS) reports that accidental domestic poisoning by the CO affects about 1000 households [3], and is responsible for about 100 deaths in France each year. So, both individuals and industrials interests on that topic have led to the development of new solutions to measure carbon monoxide concentration in the air [3][4].

In this paper, a new type of carbon monoxide sensor relying on nitrogen-based macrocyclic molecules that show a great affinity towards this gas is studied. We firstly present experimental data to attest the efficiency of cobalt corroles to trap CO molecules with high selectivity, and secondly, we establish the capability of a Surface Acoustic Wave (SAW) device to probe the mechanical properties of the corroles layer to reveal the adsorption of the target gas. Among the technologies available, we chose the SAW devices for their ability to deliver real time response, low power consumption, high sensitivity to gravimetric perturbation, stability and eligibility in wireless sensor [5][6][7]. Their intrinsic lack of selectivity represents the major disadvantage of this technology. But we intend to overcome that issue by the association with highly selective cobalt corroles. Indeed, the robustness of SAW devices in delay line configuration allows for the deposition of a selective layer compatible with its normal operation [8][9]. Finally, we propose a differential configuration for the sensor to overcome the sensitivity to outer parameters and interferent gases. In that purpose, a reference device based on copper corroles was implemented as part of the sensor. Measurements of carbon monoxide concentration in the 100-7000 ppm range in the presence of major interferents, such as O_2, CO_2 and H_2O (humidity) were achieved. Based on the experimental results, we have shown the capability of cobalt corroles as sensing material as well as the interest of copper corroles as part of a reference device to improve the stability of the phase signal. The advantage of the differential configuration in terms of sensitivity and repeatability of the measurements is discussed as a conclusion.

In Section II, we describe the configuration and manufacturing of the SAW device as well as the gas sorption properties of both copper and cobalt corroles used for the functionalization of our sensor. In Section III, we show CO measurements, in presence of major interferents, that emphasize the advantage of the differential configuration. In the conclusion, based on the presented data, we highlight the validity of our approach for the development of a selective CO sensor.

II. MATERIALS AND METHODS

In this section, the design and fabrication of the SAW device are briefly described as well as the surface functionalization process. The sorption properties of metallocorroles are also exposed emphasizing their interest for the functionalization of the sensor's surface.

A. Surface Acoustic Wave sensor

In designing our sensor, we chose a double delay line configuration allowing for differential measurement. Fig. 1 shows the geometry of the sensor composed of these two delay lines. Both lines are composed of two Inter-Digitated Transducers (IDT) for both generation and detection of the acoustic wave at the input and output of the delay line. The IDTs are made of aluminum deposited on YXl36 quartz and shaped by mean of a lift-off process using negative photoresist. In order to allow the Love-mode acoustic wave to propagate at the surface of the device, a silica guiding layer is deposited by mean of a PECVD technique on top of the IDTs. Both IDTs consist of 50 splitted finger pairs with a grating period of 10 µm yielding an acoustic wavelength equal to 40 µm. The aperture of the delay lines represents 75 wavelengths and the propagation path length is 5 mm. As the wave velocity approaches 5100 $m.s^{-1}$, the frequency operation is in the vicinity of 125 MHz.

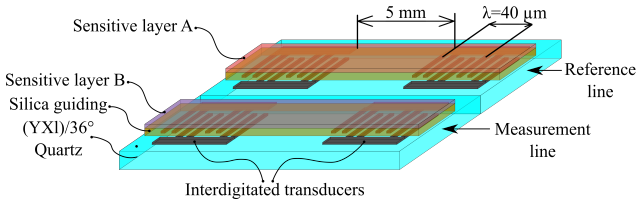

Figure 1: SAW device used for the manufacturing of the gas sensors.

The first line is coated with cobalt corroles, described in the next section, which allows for the selective trapping of carbon monoxide. The second line is coated with copper corroles, which does not show affinity to carbon monoxide. The first will be used to measure the target gas concentration and the second will be used as a reference for this measurement. The deposition of the metallocorroles is achieved by mean of a spray-coating technique. To ensure the reproducibility of the deposition process, the amount of corroles deposited on the SAW's surface is monitored by mean of the gravimetric sensitivity of the SAW sensor.

B. Metallocorroles as functionalization layer

The metallocorrole [5,10,15-tris(2,6-dichlorophenyl) corrolato]cobalt(III), named here cobalt corrole, was synthesized as already described in our previous work [10]. The reactivity of the complex was studied by adsorption measurements in static and dynamic conditions. The gas adsorption isotherms for CO, O_2 and CO_2 recorded at 298 K are shown in Fig. 2a. Solid lines represent the fitting curves using a triple-site Langmuir model for CO and a single one for O_2 and N_2. The isotherms show that the cobalt corrole presents a high CO uptake and low adsorption capacities for N_2 and O_2. For these two last gases, the uptake values are respectively equal to 1.9 $cm^3.g^{-1}$ and 4.8 $cm^3.g^{-1}$, respectively. The cobalt corrole shows a CO sorption volume equal to 21.9 $cm^3.g^{-1}$ (2.7% (w/w)) at 1 atm and the isotherm can be described by a combination of two different processes. The first one is assigned to an adsorption phenomenon with a high affinity in the low-pressure range (0-0.05 atm) thanks to the coordination of one carbon monoxide molecule on the cobalt center. These outcomes make cobalt corroles an suitable compound for the functionalization of the measurement line.

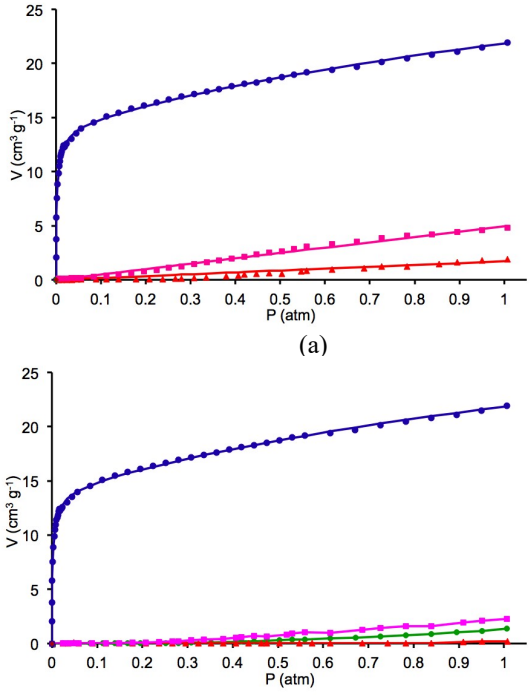

Figure 2: a) Adsorption isotherms of CO (blue), O_2 (pink) and N_2 (red) for cobalt corrole recorded at 298 K. Solid lines represent the fitting curves using a triple-site Langmuir model for CO and a single one for O_2 and N_2 ; b) Adsorption isotherms of CO (blue) for cobalt corrole compared to CO (green), O_2 (pink) and N_2 (red) for copper corrole recorded at 298 K.

In view to design a differential configuration of the sensor, the use of an accurate organic layer with no affinity for CO is required as a reference sample using a two delay lines system (vide infra) in order to reduce the outer parameters as well as interfering compounds. As a result, the copper complex [5,10,15-tris(2,6-dichlorophenyl)corrolato] copper(III) was chosen for the reference line, since this complex shows no sorption properties of CO (Fig. 2b).

III. RESULTS AND DISCUSSION

Fig. 3 shows the signal on the measurement line functionalized with cobalt corroles (red curve) and the reference line covered with copper corroles (blue curve). One can notice a drift of the phase attributed to outer parameters. The black curve represents the differential signal

obtained by subtracting the phase of the reference to the phase of the measurement line. This differential signal (green curve) shows the compensation of the phase drift that results in a stable basic level of the signal.

Fig. 4 shows a serie of measurements of CO concentrations in various conditions with (Diff) and without (Raw) the use of the differential system. We notice a dramatic reduction of the measurements dispersion when using the differential system. A statistical characterization of these data reveals that the standard deviation induced by CO_2 at 20 000 ppm is reduced by a factor 4.5 compared to an ideal case in pure nitrogen. In the case of oxygen at 20%, which is one of the main interferents, the deviation is greatly reduced by a factor 30. These results emphasize the interest of a differential configuration of the sensor to improve the repeatability of the measurements. It also strengthens our will to synthesize organic compounds for the development of a well-designed reference line.

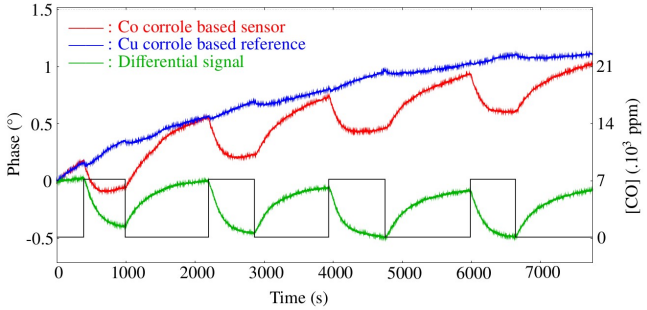

Figure 3: Comparison between phase signals from the measurement line (in red), the reference line (in blue) and the differential signal (in green).

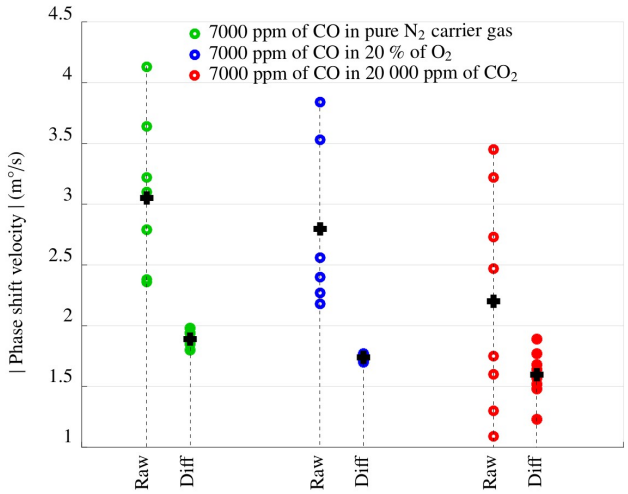

Figure 4: Influence of the differential acquisition on the repeatability of the measurements of 7000 ppm of CO in various carrier gases. Raw data represent the signal from the measurement line and the Diff data the differential signal. The mean value is represented by the cross.

The impact of O_2 and CO_2 at high concentration have been determined. As expected from previous works [11], a linear correlation between CO concentration, from 100 ppm to 7000 ppm, and the phase shift velocity undergone by the sensor is observed. Experimental results, presented in Fig. 5, show that this linear behavior stands regardless of the composition of the carrier gas for both measurement line and differential sensor. From there, the sensitivity of the sensors could be determined. In pure nitrogen, the measurement line sensitivity is 263±124 n°/s/ppm. The uncertainty on the sensitivity drops dramatically in the case of the differential sensor for which the sensitivity is 238±6.5 n°/s/ppm. It appears that in the presence of 20% of oxygen the uncertainty remains equivalent for both sensor configurations. In the presence of CO_2 at 20 000 ppm the measurement line sensitivity is 166±29 n°/s/ppm while the differential sensor exhibits a selectivity of 225±3 n°/s/ppm. The same characterization was made in the presence of water in the carrier gas and a spectacular difference between the raw measurements without reference and the differential acquisition has been observed. As shown in Fig. 5, the uncertainty on the sensor sensitivity is divided by 50 with the use of a differential acquisition.

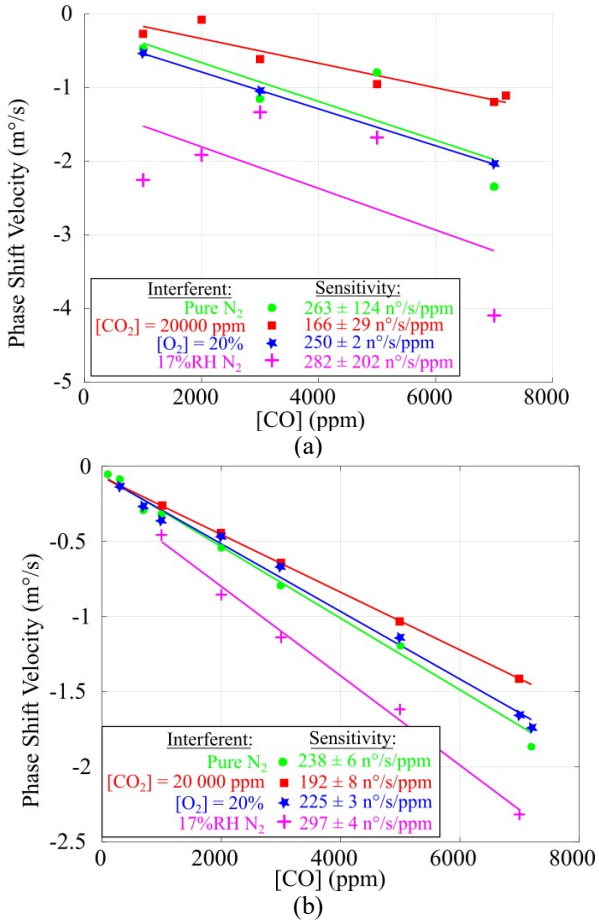

Figure 5: a) Measurement line sensitivity in presence of oxygen (blue), carbon dioxide (red) and humidity (pink) on the carrier gas. b) Differential sensor's sensitivity in the presence of the same interferent.

The effect of the other pollutant gas, such as H_2 or H_2S, on the sensor selectivity will draw our attention in further works. Even if the quartz substrate used for the manufacturing of the sensor is a temperature compensated AT-cut, a sensitivity to temperature may rise from the functionalization of the device. The effect of temperature on the sensor stability will, consequently, provide a focus of work.

IV. CONCLUSION

In this research, we developed an original sensor for carbon monoxide monitoring based on a SAW device and metallocorroles. This approach takes advantage of the intrinsic high sensitivity to gravimetric phenomena of SAW sensors, combined with CO selective sorption capabilities of the cobalt corroles. Copper corroles have been exploited for the development of a dedicated reference line. We have shown that the use of a proper reference line as part of a differential sensor provides improvement in the repeatability of the measurements and allows for the diminution of the uncertainty in the sensor sensitivity. These results pave the way for the detection of other gases with acoustic waves devices associated with dedicated functionalization compounds for the development of a multi-gas monitoring system.

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