Love Wave Sensors Functionalized with Cobalt Corroles or Metalloporphyrines Applied to the Detection of Carbon Monoxide

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Abstract - **This article described highly sensitive gas sensors for monitoring low ppm or ppb concentrations of carbon monoxide using phase variations at constant frequency of Love waves generated by a surface acoustic wave device. The sensing material for gas detection employed in this study is a silica layer modified with one of three compounds that assure a selective trapping of CO. The authors demonstrate that surface acoustic wave devices with non-conductive sensing layers as described can be used for molecular recognition such as to detect carbon monoxide molecules. This article reported an interest and original work.**

Keywords- CO detection; SAW device; porphyrine; cobalt corroles.

I. INTRODUCTION

Carbon Monoxide (CO) is produced by incomplete combustion. Because of its intrinsic properties, it is naturally undetectable by human body. His toxicity and undetectability make him a dangerous compound. This observation leads to the necessity of developing a device able to detect the presence of CO in the air.

The strong demand for the development of lab-on-chip analysis devices has pushed to investigate many different approaches in that matter. Among these, the use of surface acoustic waves has received a particular interest during the last decade. Specially, pure shear guided waves in stratified substrates such as amorphous silica on quartz allowing for the use of Love waves appears as an attractive solution to fabricate devices able to operate in water, since shear waves are not radiated in fluids and because of their noticeable sensitivity to gravimetric effects related to surface adsorption. Many devices based on delay line configurations have been built and tested with various successes. However, the use of resonators instead of delay lines is expected to provide better sensing capabilities particularly when monitoring phase shifts at constant frequency due to gravimetric effects. For Surface Acoustic Wave devices (SAW), mass sensitivity is given by the Sauerbrey relation (1).

$$S_m = \frac{\Delta f}{f_0} \cdot \frac{A}{\Delta m} \qquad (1)$$

where f_o is the resonance frequency of the unperturbed SAW sensor, A is the active area, Δm and Δf are mass and frequency variations, respectively. SAW devices working at 125 MHz are used in these developments. The sensibility of these devices is about 250cm²/g.

Besides, a great variety of artificial receptors particularly useful for chemical sensors development have been fabricated, benefiting from progresses of synthetic chemistry methodologies. SAWs (Fig. 1) have allowed for demonstrating the exploitation of CO molecular trapping occurring in non-conductive sensing layers [1]. We propose in this paper to compare the performance of different compounds used as sensing layer. We have monitored phase variations of SAW devices, functionalized with three different sensing layers, when loaded with CO molecules. The three tested compounds are cobalt corroles [5,10,15-Tris(2,6-dichlorophenyl) corrolato]Co(III)] (Fig. 2) [2] and two metalloporphyrines [Fe(II)-(5,10,15,20-tetrakis(3,5-dihydroxyphenyl)porphyrin] [3, 4] referred as porphyrine #5 and [5,10,15,20-tetrakis (3,5-dimethoxyphenyl) porphyrin) Mn(III)] referred as porphyrine #6 (Fig. 4) .

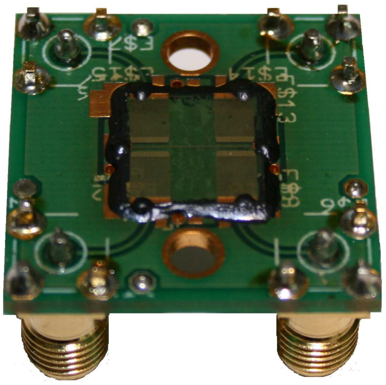

Figure 1. SAW device

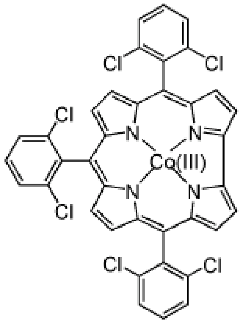

Figure 2. Scheme of a cobalt corrole [5,10,15-Tris(2,6-dichlorophenyl)corrolato]cobalt(III)])

II. EXPERIMENTS

For Love-wave-based sensors, since the acoustic wave generated by the transducers is mainly a surface acoustic wave, it reveals extremely sensitive to perturbations occurring at the surface of the device. Modification of the acoustic wave propagation conditions in the silica guiding layer leads to the modification of the physical characteristics of the wave. During the tests, CO sensors have been exposed to changes of several experimental parameters (temperature, flow, pressure, presence of gas). In order to exclusively extract the information concerning CO adsorption, we used a specific differential setup comprising two SAW devices. In contrast to previous experiments [1][3] the experiments were conducted at atmospheric pressure to more closely simulate sensor application conditions. To this end, a dedicated gas test setup, optimized for CO detection, has been developed.

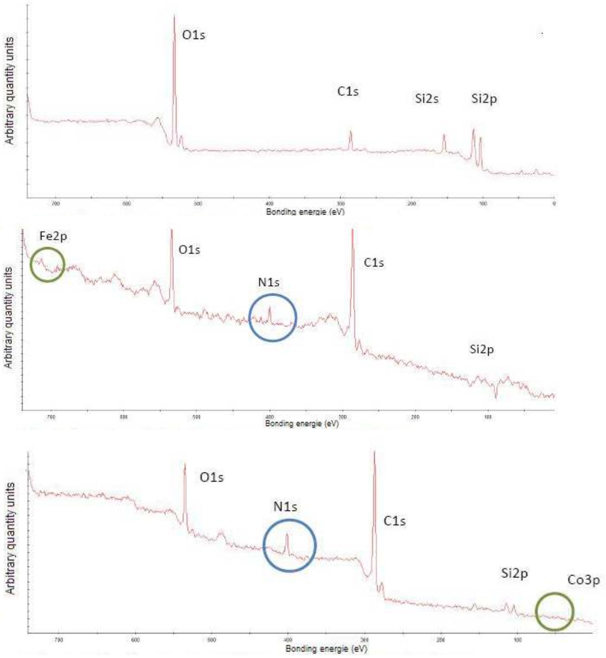

Figure 3. X-ray spectra of SAW devices before functionalization deposition (first); after porphyrines #5 spray coating (second); after cobalt corroles spray coating (third)

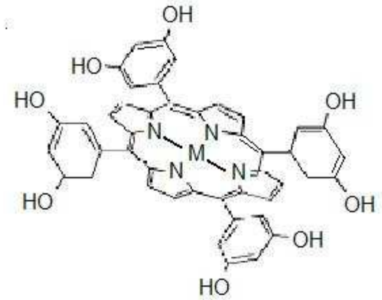

Figure 4. Scheme of an organometallic prophyrin (M: central metal atom) M-(5,10,15,20-tetrakis(3,5-dimethoxyphenyl)porphyrin)

A crucial point of the development of SAW sensor is the functionalization of its active surface with chemical treatment able to assure the selective trapping of CO. Sensing layers were synthesized following literature methods [2][4][5]. Prophyrins and cobalt corroles were dissolved in a proper solvent (10^{-3} M in $CHCl_3$) and deposited by spray coating. Love-wave devices used, consists in delay lines built on (AT, Z) cut of quartz. The wave guidance is achieved by depositing a 2.5 µm thick silica overlay onto the InterDigited Transducers (IDTs) and the propagation path as well. The Love wave is generated and detected using IDTs composed of 50 pairs of 4-finger-per-wavelength electrodes made of 200 nm thick evaporated aluminium.

In order to ensure the presence of the functionalization, we made a XPS (X ray Photon Spectroscopy) analysis of the surface of SAW devices before and after the deposition of cobalt corroles and porphyrines. A few spectra are reported here. The resulting wide scans are presented in Fig. 3. The raising of two peaks characteristic of the presence of silicon (Si2p and Si2s), oxygen (O1s) and the presence of small peaks of carbon due to pollution can be observed on the bare device's spectrum showing the absence of functionalization onto the silica composed surface. After cobalt corroles deposition, we note the augmentation of the carbon peak and the appearance of two peaks showing the presence of nitrogen and cobalt. A decrease of O1s and silicon intensity peaks has been observed. This tends to prove that a thin film has been effectively deposited onto the surface. The apparition of a nitrogen peak also confirms the presence of an overlay onto the silica surface due to four atoms of nitrogen surrounding the organometallic atom. Analyses of devices that have been covered with porphyrines #5 and #6 show Fe and Mn organometallic peaks. The oxygen peak is still higher than in presence of corroles due to –OH groups on both. The XPS analysis has yield evidences of the deposition of the two compounds onto the SAW device's surface. It has also allowed for the chemical characterisation of these functionalizations.

An experimental bench has especially been developed for high sensitivity detection of CO (Fig. 5). In order to proceed to differential acquisition [6] allowing for minimizing the influence of changing experimental parameters preventing

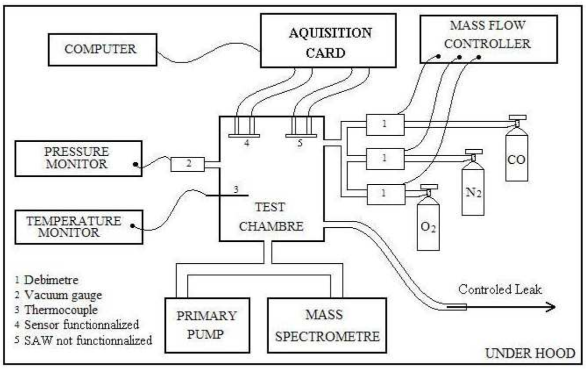

Figure 5. Scheme of our specific cell for toxic gas detection.

the CO detection, two sensors are used. One coated with corroles sensitive to CO [1][2] and the other non-functionalized used as a reference.

The cell is equipped with three mass flow meters driven by a controller allowing the dilution of CO with N_2 and O_2. Moreover, a primary pump provides vacuum conditions that permit a faster regeneration of the sensitive area of the sensors, making it reusable.

III. MOTIVATION AND RESULTS

We report here the results obtained for CO detection using SAW devices functionalized with cobalt corroles and metalloporphyrines, which reversibly interact with gaseous analytes by coordination with the central metal atom. One can see in Fig. 6 the trend of a phase variation due to CO adsorption onto the surface of a device functionalized with cobalt corroles. The experiments have been achieved at least three times to validate the results. We obtained the same trends with devices functionalized with porphyrines, with slightly different slopes. In every case, we confirm reversibility of the adsorption. We have monitored the respective phase shift velocity undergone by the Love wave, propagating within the guiding layer of the devices functionalized with each compounds, versus the CO concentration of the gas injected in the test cell and confirm a linear correlation (Figure 7, 8 and 9).

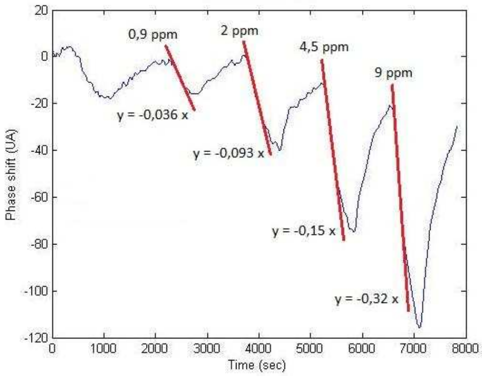

Figure 6. Phase variation due to CO adsorption onto the SAW device surface.

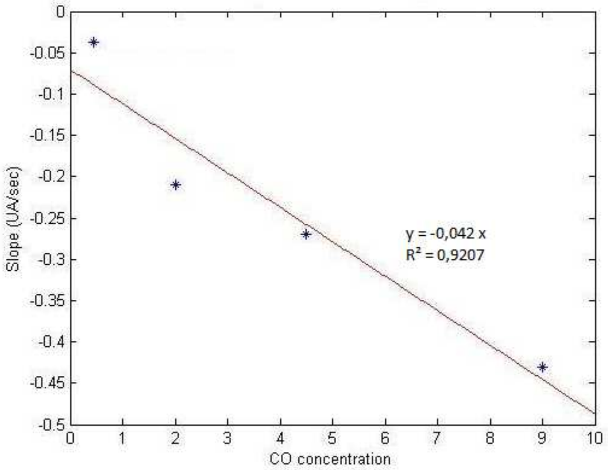

Figure 7. Graphic representation of the phase shift velocity obtained with porphyrine #5 versus CO concentration at atmospheric pressure.

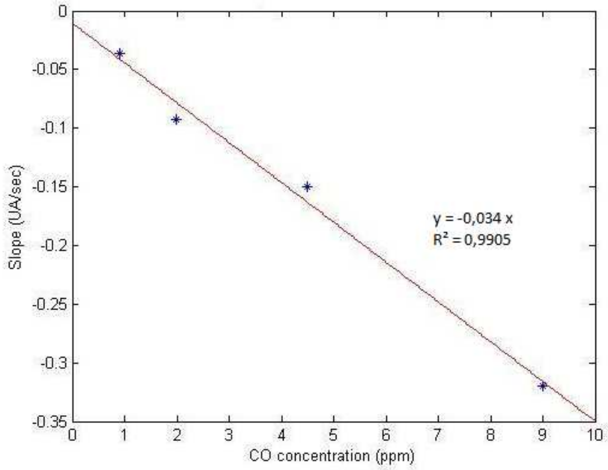

Figure 8. Graphic representation of the phase shift velocity obtained with cobalt corroles versus CO concentration at atmospheric pressure.

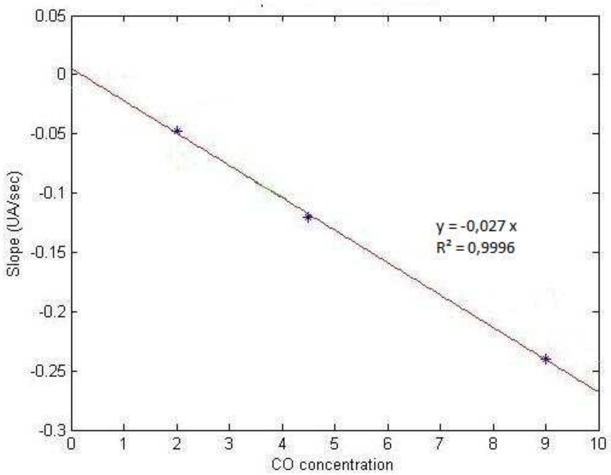

Figure 9. Graphic representation of the phase shift velocity obtained with porphyrine #6 versus CO concentration at atmospheric pressure.

TABLE I. FUNCTIONALIZATIONS PERFORMANCES

	Functionalization type		
	Porphyrine n°5	***Cobalt corroles***	***Porphyrine n°6***
Detection threshold	450 ppb	900 ppb	2ppm
Corresponding phase shift velocity	-0.04 UA/s [a]	-0.05 UA/s [a]	-0.05 UA/s [a]

a. UA: Arbitrary Units

Porphyrine #6 enables us to detect at least a CO concentration of about some ppm. With cobalt corroles, the detection threshold is situated below one ppm. We note that the porphyrine #5 provides a clear detection of a minimum of 450ppb CO concentration [Table I].

We also note that the phase shift velocity induced by the injection of 900ppb with porphyrine #5 is about four times higher than with corroles. This reflects the highest sensitivity of porphyrine #5 with CO.

Since porphyrine #5 induces phase shifts velocity four times larger than what we get with cobalt corroles we can conclude that this compound represents the preferred solution for CO detection at atmospheric pressure.

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