Detection and monitoring of carbon monoxide using cobalt corroles film on Love wave devices with delay line configuration

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Abstract

Among specific sensitive materials synthesized for chemical sensor development, cobalt corrole have shown attractive capabilities for CO detection [1, 2]. In this paper, we investigate the possibility to exploit such materials to develop surface acoustic wave (SAW)-based sensors. We actually demonstrate that SAW devices using delay line configuration allow investigating the molecular recognition occurring in non-conductive sensing layers of cobalt corroles. We have monitored phase variations of SAW devices versus various CO concentrations. Moreover, a specific testing setup has been developed to precisely dose CO at low concentrations, to avoid any CO leakage in the environment, to systematically control environmental parameters and to allow regeneration of the trapping sites of CO.

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Keywords: CO detection; SAW device; cobalt corroles.

1. Introduction

Carbon Monoxide (CO) is produced by incomplete combustion. Those physical properties are so that it is a colorless and odorless compound. His toxicity and his undetectability make him a dangerous compound which is known as the “silent killer”. This observations lead to the necessity of developing such 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.
Especially 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 make the detection of gravimetric effects related to surface adsorption. For SAW devices, mass sensitivity is given by the relation (1) according to the Sauerbrey equation [3, 4]:

\[
S_m = \frac{\Delta f}{f_0} \frac{\Delta m}{A}
\]  

(1)

where \(f_0\) is the resonant frequency of the unperturbed SAW sensor, \(A\) is the active area, \(\Delta m\) and \(\Delta f\) are mass and frequency variation, respectively. In our case, with a SAW sensor working at 125 MHz, mass sensitivity is ten times more sensitive than QMB (Quartz MicroBalance) (that is to say: 25 cm².g⁻¹). Here we investigate on gas sensors based on Love wave devices, which give the means to exploit the molecular recognition events occurring in non-conductive sensing layers composed of cobalt corroles. This compound is able to assure the trapping of CO onto the device’s surface.

2. Equipment and devices

These SAW devices consist in delay lines built on (AT, Z) cut of quartz (Fig. 1a). A 2.5 \(\mu\)m thick silica overlay is deposited onto the interdigitated transducers (IDTs) providing a propagation path which permit the guidance of the acoustic wave. The Love wave is generated and detected using IDTs composed of 50 pairs of electrodes (4-finger-per-wavelength) made of 200 nm thick evaporated aluminum. The grating period is 10 \(\mu\)m, i.e. a wavelength close to 40 \(\mu\)m yielding a frequency operation in the vicinity of 125 MHz as the wave velocity approaches 5000 m.s⁻¹. In order to make a differential acquisition, one bare device is used as a reference and the other one is functionalized with cobalt corroles by means of spray-coating.

A crucial point of the development of SAW sensor is the functionalization of its surface with \([5,10,15\text{-Tris}(2,6\text{-dichlorophenyl})\text{corrolato}]\text{cobalt(III)}\]) named cobalt corroles (Fig. 1b) able to assure the selective trapping of CO. This compound interacts with CO molecules by coordination to the central metal atoms. In addition, it exhibits a remarkable affinity and selectivity for CO vs. O₂ and N₂ [2].

In order to avoid the contamination of the working environment, a specific test bench has been developed (Fig. 2) with several monitors to control pressure, temperature and flow. To get close to conditions of use of such a sensor, we performed experimentations at atmospheric pressure. The bench also permit to get vacuum conditions to promote desorption of the gas from the surface between every measurements. Mass flow controllers permit the use of N₂ and synthetic air for the dilution of CO gaz.
3. Measurement

The raising of mass at the surface of the device leads to a phase variation at constant frequency and a shift of the resonant frequency toward the low frequencies. A dedicated and fully software-controlled instrumentation to monitor delay lines in an open-loop configuration has been used for data acquisition. This instrumentation features high stability and measurement accuracy and has been used for the preliminary characterization of the transfer function of sensors and for selecting the optimum working frequency used for the gravimetric detection [6].

During experiments, the CO sensor is exposed to several variations of experimental conditions (variation of pressure, presence of water vapor, variation of temperature, presence of gas...). In order to extract the information concerning CO adsorption, we used a specific differential setup comprising two SAW devices. Fig. 3 a&b respectively show the response of the bare device used as a reference and the functionalized one, coated with Co corroles. By subtracting the response of this reference to the response of the functionalized device, we are able to get the phase shift due to the only phenomenon of CO adsorption. The differential signal of the phase variations of the acoustic wave under N₂ and CO flow is presented in Fig. 3c.

![Fig. 2. Scheme of the test bench used for dilution and monitoring of the CO concentration.](image)

![Fig. 3. Phase variation under gas flow of the bare device (a) and the functionalized device (b); differential signal (c).](image)
4. Experiments and results

Love-wave-based sensors reveal extreme sensitivity to modifications of the conditions of propagation of the wave in the silica guiding layer. In fact, we know that the raising of mass at the device’s surface leads to a shift-down of the synchronism frequency. Since the phase variation is linear with the frequency, the shift-down of the transfer function due to mass adsorption can be detected by a phase shift at constant frequency. Figure 4a shows the differential signal of the phase variations of the acoustic wave under CO flow. We can notice that in order to characterize the adsorption of CO onto the surface, we monitor the slope at the beginning of the decrease of phase at constant frequency. This measurement permits the detection with response time of a few seconds.

The experiments have been repeated several times to validate the results. Successive injections of lower and lower concentrations of CO were realized to determine the limit of detection of our sensors. The repeatability of our measures is made by realizing three series of injection with concentrations of CO going from 9 to 0.45ppm. We observed a linear correlation between sensor response slopes and the applied CO concentrations in each measurement series (figure 4b). Every series of measures allowed to obtain coefficients of correlation superior to 0.95ppm. The first measures were realized under vacuum and then performed at atmospheric pressure under a constant flow of nitrogen. It was finally performed at atmospheric pressure in presence of synthetic air.

Fig. 4. (a) phase variation of the sensor device under CO flow; (b) graphic representation of the phase shift velocity versus CO concentration at atmospheric pressure with nitrogen used for dilution

These encouraging results, obtained with our new experimental setup, pave the way to investigate other acoustic wave’s devices, such as STW resonators, to reach lower detection thresholds.

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