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Development of Love Wave devices based on delay line configuration for the high detection and monitoring of carbon monoxide

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In this paper the properties of gas sensors based on surface acoustic wave devices (SAWs) are investigated. This device give the means to exploit molecular recognition events occurring in non-conductive sensing layers composed of cobalt corroles [5,10,15-Tris(2,6-dichlorophenyl)corrolato]cobalt(III)]. Phase variations for SAW were monitored and detection efficiency was studied. Moreover, a specific cell, for gas dilution, was developed to avoid the contamination of the working environment and to perform the regeneration of the device by freeing CO trapping sites. With functionalized SAW devices, CO concentrations of some tens of ppm have been detected. These encouraging results with SAW sensors pave the way to detection and measurement of sub-ppm concentrations.

1 Introduction

Carbon Monoxide (CO) is produced in various industrial and current-life processes by incomplete combustion of organic materials. It is a colorless, odorless, tasteless and toxic gas that is highly reactive with living tissues. Because of its properties, it is naturally not detectable by human olfaction. Its toxicity and undetectability make it a dangerous compound known as the “silent killer”. This observation leads to the necessity of developing devices able to detect the presence of CO in the air. A crucial point of the development of such sensors is the functionalization of its sensitive surface with chemical processing allowing the trapping of CO molecules. In this context, new materials such as metallo-corroles have been developed [1-3]. In CO poisoning, the toxic molecule coordinates with the iron ion located at the centre of the haemoglobin protein. Cobalt (III) corroles also interact with CO by coordination to the cobalt central metal atom.

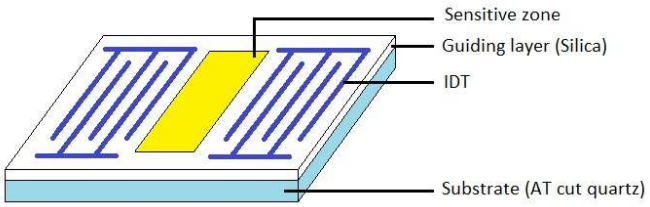
In principle, gravimetric sensors disregard the electronic properties of the absorbing layer; only the mass variations are detected by the molecular adsorption. Among gravimetric sensors, quartz microbalances are the most exploited components for their simple preparation and operation. However, the development of lab-on-chip analysis devices is currently expected as another way to investigate different solutions on that topic. Surface acoustic waves (SAW) have so received a strong interest during the last decades for gravimetric detection.

In this paper, the properties of gas sensors based on Love wave devices that can accurately detect a toxic gas concentration in atmosphere are investigated by using the properties of non-conductive sensing layers. By using functionalized SAW devices, we observe a few second time responses when switching from air to CO polluted atmosphere, with a phase shift several times larger than the baseline noise level. The theoretical background of the proposed development is first presented with a brief recall of the sensor and system operation principles. The device functionalization and experimental assessment of the system operation as well and result discussions are then reported, preceding the paper's conclusion.

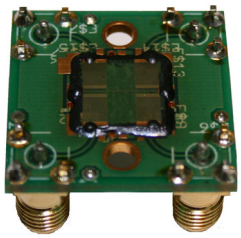
2 Experiments

- 2.1 Manufacturing of the sensor

Love-wave devices (Fig.1a&b) consists in delay lines built on (AT,Z) cut of quartz. The Love wave is generated and detected using piezoelectric properties of quartz by IDTs composed of 50 pairs of electrodes (4-finger-per-wavelength) made of 200 nm thick evaporated aluminum. The grating period is 10 µm, i.e. a wavelength close to 40µm yielding a frequency operation in the vicinity of 125MHz as the wave velocity approaches 5000m.s^{-1}. A 2.5µm thick silica overlay is deposited onto the interdigited transducers (IDTs) providing a propagation path which permit the guidance of the acoustic wave with a minimum loss of the acoustic energy along the propagation.



a)



b)

Figure 1: a) Schema of delay line configuration
b) Photograph of the SAW sensor

- 2.2 Functionalization of the SAW sensor sensitive area

The sensitive layers deposited onto the devices used here are composed of cobalt corroles (Fig. 2.). In previous studies [4] the CO trapping capability of different compounds such as porphyrines have been investigated. The corroles are preferred since it presents a stronger coordination of the CO molecule with the cobalt atom at the centre of the macrocycle and does not decompose when exposed to humidity [2]. This behaviour fits well with the long term use of a sensor.

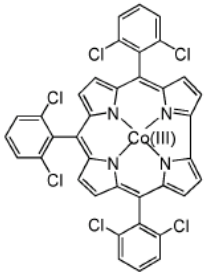


Figure 2: Cobalt corroles used for the functionalization of the sensors

Thin films of this compound were deposited onto the surface of the delay lines by spray coating. Cobalt corroles [5,10,15-Tris(2,6-dichlorophenyl)corrolato]cobalt(III), were dissolved in a proper solvent at 10-3 M in dichloromethane. The amount of deposited Metallocorroles was measured on-line during the deposition process via a high stability frequency counter.

- 2.3 gas sensing setup

It has been shown that the cobalt corroles can trap carbon monoxide by coordination to the central cobalt atom. Moreover, these compounds exhibit a remarkable affinity to CO versus O2 and N2 that are the two main compounds that compose the atmosphere of the sensor when used in standard conditions.

The interaction between the corroles and the gas to detect is reversible and its property is improved by the application of vacuum conditions in the atmosphere of the sensor when exposed to carbon monoxide. Consequently, the test bench has been developed to allow for placing the reaction chamber under primary vacuum conditions to promote the regeneration of the CO trapping sites. During the tests, Love-wave-based sensors are exposed to changes of several experimental parameters (temperature, flow, pressure, presence of gas). In order to extract the information concerning CO adsorption, a specific differential setup is used. This differential measurement requires two delay lines composing the sensor. One of these delay lines is kept clean as a reference and the other one is covered by spray coating with cobalt corroles yielding it sensitive to the presence of CO. The response of the bare device and the functionalized one are respectively measured. A dedicated instrument based on a full software control has been developed providing stability and accuracy of the measures [5]. By this way, influence of experimental parameter changes limiting or even preventing the CO detection is minimized. In figure 3, the experimental test bench specially designed for high sensitivity carbon monoxide detection is presented.

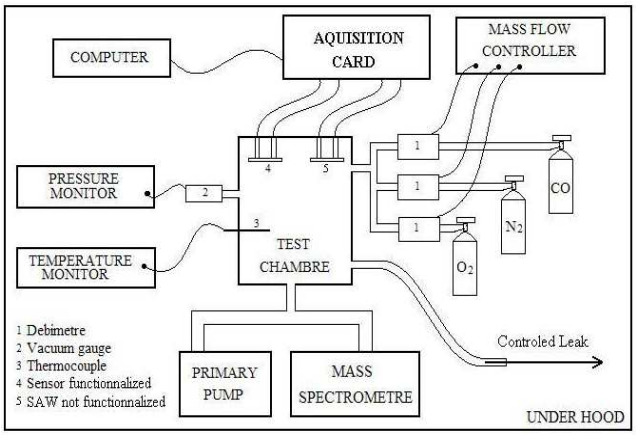


Figure 3: Scheme of our specific toxic gas detection cell.

3 Results and discussion

Since the acoustic wave generated by the transducers is a surface acoustic shear wave with a horizontal polarization, it reveals extreme sensitivity to perturbations occurring at the surface of the device. Any modification of the acoustic wave propagation conditions inside or above the silica guiding layer perturbs the physical characteristics of the wave and more specifically its phase velocity. Using a network analyzer, one can determine the transfer function of the device and hence monitor the phase shift induced by mass adsorption within the sensitive layer. By this way, information about the CO loading onto the device's surface is simply and rapidly obtained. By a matter of fact, increasing the deposited mass at the device's surface leads to a shift-down of the delay line synchronism frequency.

Preliminary tests were performed with high CO concentration in order to check the device signal dynamics when loaded with a maximum concentration of the tested gas. The toxicity of CO at such concentrations being so high, experiments were led under vacuum to avoid any leakage in the working environment. These firsts results showed that the measurement of concentrations of some tenths of ppm of carbon monoxide was possible.

In order to get even closer to the final operation conditions of the sensor, the previous tests have been performed at atmospheric pressure. Knowing that the oxygen is the main compound capable to perturb the trapping of CO in the sensitive layer, nitrogen is first used for the dilutions. Figure 4 and 5 show the results relative to these experiments.

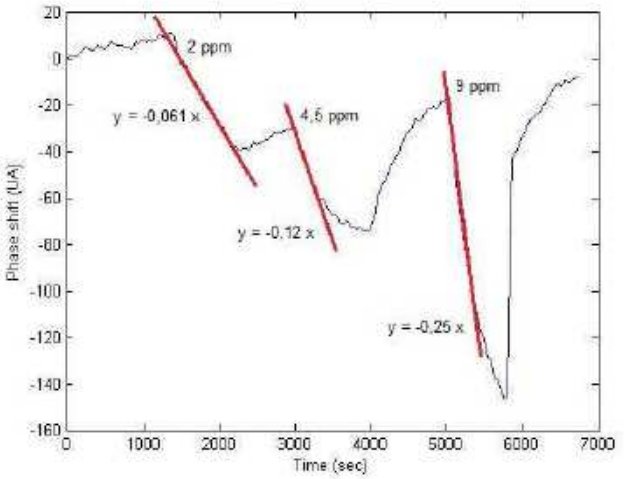


Figure 4: Phase shift measurement under atmospheric pressure and in presence of CO diluted with nitrogen.

Figure 5 shows that the sensor's response still presents a linear behavior for each series of test. Furthermore, the slope obtained on the differential signal versus the concentration of CO is nearly the same from one series to another. In addition, we emphasize that the sensitivity of the device is lower at atmospheric pressure than under vacuum, as expected. Indeed, operating at atmospheric pressure yields a 900ppb CO concentration detection barrier. This observation allows one to infer that the detection at atmospheric pressure allow the repeatability of the experiments but scarifying the sensitivity of the sensor by a factor of 2.

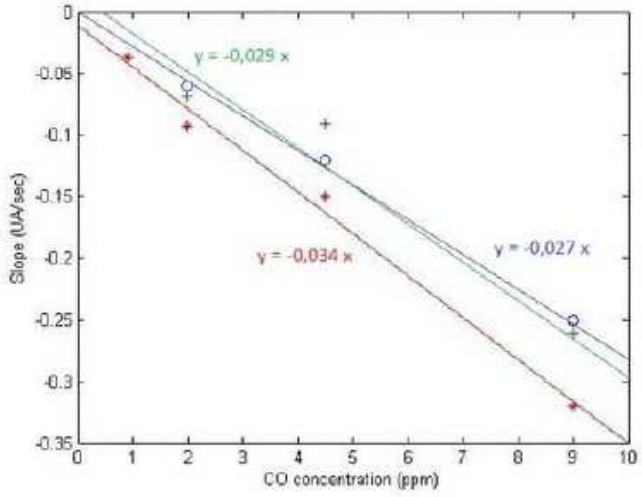


Figure 5: Phase shift velocity under atmospheric pressure VS concentration of CO.

Still in the purpose of approaching the actual working conditions of the sensor, the later has been tested under atmospheric pressure in presence of air. Exposing the sensor to the air before the injection of CO can also validate the fact that cobalt corroles are able to coordinate CO molecules even if previously and simultaneously exposed to oxygen. The air used for this experiment has been synthesized from pure oxygen and pure nitrogen. Figures 6 and 7 report the observations made concerning the capability of the sensitive layer to adsorb CO in presence of oxygen.

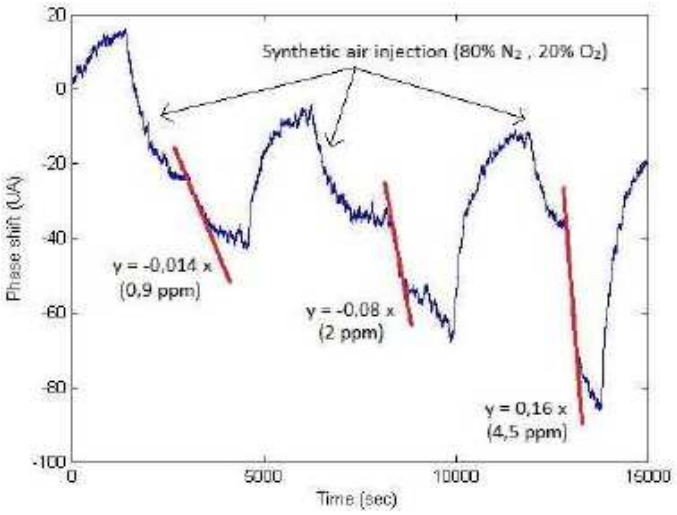


Figure 6: Phase shift measurement at atmospheric pressure and with CO diluted in synthetic air.

As shown in Figure 7, the use of the sensor in presence of air does not degrade the detection threshold of the device and therefore a 900ppb detection barrier is also met. However, the repeatability of the experiment was not observed in the present case.

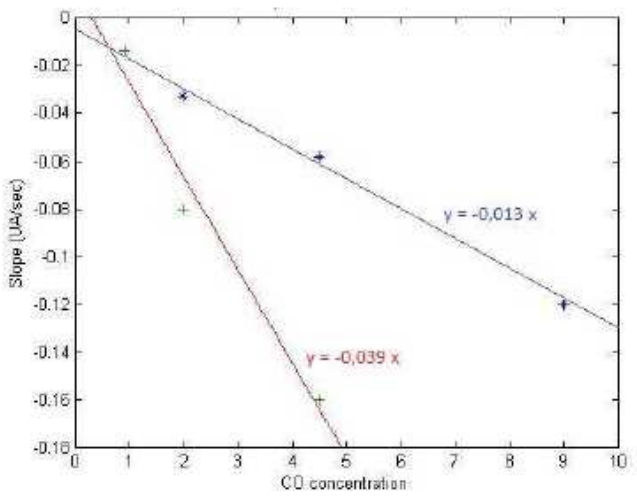


Figure 7: Phase shift velocity under atmospheric pressure VS concentration of CO diluted in air.

4 Conclusion

As a conclusion, the use of surface acoustic wave device coupled with the exploitation of new materials for the selective trapping of carbon monoxide enables one to detect, measure and monitor a wide range of CO concentrations. Indeed, the use of cobalt corroles combined with acoustic devices based on Love waves using quartz substrate operating at 125MHz has allowed for selective detection of ppm concentrations of carbon monoxide. In addition, a test bench has been developed to perform the detection under controlled conditions of pressure, temperature and gas flow. The obtained results are promising and pave the way to sub-ppm CO concentrations measurements. In order to improve our detection device, studies concerning the deposition process of the sensitive layer are engaged. Moreover, the use of acoustic resonators working at higher frequency will be tested as it is expected to increase the mass sensitivity and the signal/noise ratio.

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