Functionnalized Surface Acoustic Wave Sensors for the Detection of Hazardous Gases

Meddy Vanotti
Time and frequency Department, FEMTO-ST Institute
26 ch. de l'Epitaphe 25030 Besançon, France
Email: meddy.vanotti@femto-st.fr

Christophe Théron
NIMBE, UMR 3685, CEA, CNRS,
Université Paris-Saclay, CEA-Saclay
91191 Gif-sur-Yvette, France
Email: theronchris@gmail.com

Valentin Quesneau
ICMUB, UMR CNRS 6302
9 avenue Alain Savary BP 47870 21078 Dijon Cedex, France
Email: valentin.quesneau@u-bourgogne.fr

Valérie Soumann
Time and frequency Department, FEMTO-ST Institute
26 ch. de l'Epitaphe 25030 Besançon, France
Email: valerie.soumann@femto-st.fr

Mario Naitana
ICMUB, UMR CNRS 6302
9 avenue Alain Savary BP 47870 21078 Dijon Cedex, France
Email: mario.naitana@u-bourgogne.fr

Stéphane Brandès
ICMUB, UMR CNRS 6302
9 avenue Alain Savary BP 47870 21078 Dijon Cedex, France
Email: stephane.brandes@u-bourgogne.fr

Nicolas Desbois
ICMUB, UMR CNRS 6302
9 avenue Alain Savary BP 47870 21078 Dijon Cedex, France
Email: nicolas.desbois@u-bourgogne.fr

Claude P. Gros
ICMUB, UMR CNRS 6302
9 avenue Alain Savary BP 47870 21078 Dijon Cedex, France
Email: claude.gros@u-bourgogne.fr

Thu-Hoa Tran-Thi
NIMBE, UMR 3685, CEA, CNRS,
Université Paris-Saclay, CEA-Saclay
91191 Gif-sur-Yvette, France
Email: thu-hoa.tran-thi@cea.fr

Virginie Blondeau-Patissier
Time and frequency Department, FEMTO-ST Institute
26 ch. de l'Epitaphe 25030 Besançon, France
Email: virginie.blondeau@femto-st.fr

Abstract—In this work, we show the capabilities of Surface Acoustic Wave (SAW) devices to probe the properties of gas sensitive materials for the manufacturing of hazardous gas sensors. The great capabilities of cobalt corroles for the trapping of carbon monoxide (CO) were exploited to produce selective sensors. These corroles were deposited on SAW delay lines surfaces and then exposed to carbon monoxide (CO) in standard conditions. Concentrations of a few hundreds of ppb were measured emphasizing the interest of such sensors for the detection of CO. Another type of sensitive layers exhibiting specific porosity adapted to the trapping of formaldehyde (CH$_2$O) were deposited on similar delay lines. A detection threshold of 140 ppb was shown. These encouraging results pave the way for the development of a functionalized SAW sensors network for multi-gas detection in indoor air.

I. INTRODUCTION

During the last two decades, the potential impact of indoor air quality on human health has stimulated an interest in hazardous compounds survey such as formaldehyde (CH$_2$O)[1] and carbon monoxide (CO) [2].Formaldehyde being a carcinogenic, the World Health Organization (WHO) recommends exposure limit as low as 80 ppb of formaldehyde during 30 minutes [3]. The French Institute for Health Surveillance (InVS) reports that accidental domestic poisoning by the CO affects about 1000 households in France each year [4], and are responsible for about 100 deaths. The detection of these two compounds has consequently become a need. To address these needs, we here report results on the capability of functionalized Surface Acoustic Wave (SAW) devices for the selective detection of CO and CH$_2$O.

A. Materials and Methods

1) SAW devices: SAW delay lines based on Love waves, shown in Figure 1, are used to probe mass, density or elastic properties of sensitive materials deposited as a thin layer on its surface. In this context, together with the manufacturing of the SAW device, we have developed sensitive layers capable of efficiently and selectively trap a target gas. These devices consist in two-port delay lines built on (AT, Z) cut of quartz. The Love wave is generated and detected using interdigited transducers (IDTs) composed of 50 pairs of electrodes made
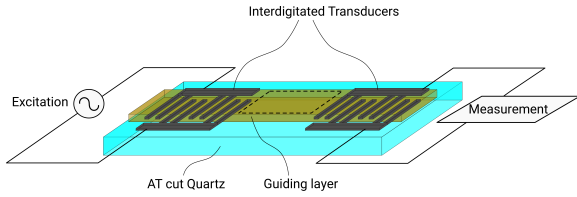
Fig. 1. Structure of the SAW device used for the manufacturing of the gas sensors. These sensors are based on a delay line configuration exhibiting a free propagation path (dotted line area) where the sensitive material is deposited.

Fig. 2. Measurements of CH_2O concentrations with SAW devices functionalized with sensitive layer L1.

of 200 nm thick evaporated aluminum. The grating period is 10 μm, i.e. a wavelength close to 40 μm yielding a frequency operation in the vicinity of 125 MHz as the wave velocity approaches 5000 m.s^{-1}. A 1 μm thick silica guiding layer is deposited onto the IDTs providing a propagation path which permit the guidance of the acoustic wave.

The electrical response of the device can be determined using a network analyzer. However, a dedicated and integrated electronics has been implemented and delivers information similar to those from a classical network analyzer. This system includes two separated phase measurement schemes: a rough characterization stage using the $AD8302$ phase and magnitude detector, and a high sensitivity phase measurement stage using dedicated phase detectors $AD9954$ with variable gain and low noise operational amplifiers as presented in another work [5].

2) Formaldehyde sensitive material: For the production of the CH_2O sensor, two different sensitive materials were tested; a first layer referred as L1 displays a specific nano-porosity allowing the trapping of small molecules such as CH_2O. A second sensitive layer referred as L2 displays functional groups aimed at improving the molecular interaction with CH_2O. Both materials were produced via the sol-gel process and were deposited as thin films on the SAW device by spin-coating. The properties of these recognition layers is not detailed here for confidentiality reasons.

3) Carbon nonoxide sensitive material: For the functionalization of the CO sensors, we took advantage of the great capabilities of cobalt corroles to trap this molecule [6], with a great selectivity toward O_2, the main interferent in CO measurement [7]. Because of the structure of the corroles, small molecules such as N_2, O_2 and CO can be trapped within by mean of weak interactions. In the particular case of CO, stronger chemical interactions are involved reaching high selectivity for this gas. The use of a variety of cobalt corroles including new structures of corroles complexes represents an innovative aspect of this work.

B. Results

Modifications of the physical properties of the sensitive layer consecutive to gas adsorption lead to a shift of the synchronous frequency of the delay line. Since the phase is linear with the frequency in the vicinity of the synchronous frequency for such a device, the frequency shift can be revealed by a phase shift measurement at constant frequency. The characterization of the adsorption of the target gas onto
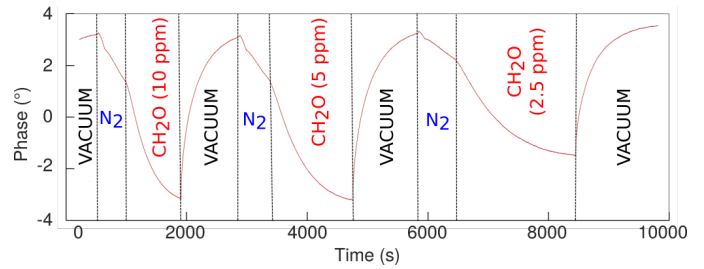
the surface is then achieved by calculating the slope of the phase at the beginning of its decrease. This approach allows to measure concentrations of gas within a few tens of seconds.

1) Formaldehyde Measurements: As shown on Figure 2, with the first layer L1 displaying a specific porosity adapted to the trapping of CH_2O, a drift of the signal in the presence of N_2 used as a carrier gas is observed indicating that N_2 molecules are also adsorbed in the nano-porous layer. This lack of selectivity induces a weak sensitivity of the sensor to CH_2O. As a matter of fact, it enables the detection of CH_2O only at concentrations superior or equal to 2.5 ppm which do not fit with the required WHO detection threshold.

Based on these results, the second functionalized sensitive layer L2 have been used to enhance CH_2O adsorption at the expense of N_2 adsorption. One can see in Figure 3(a) that with L2, the drift caused by the exposure to N_2 is substantially reduced and the sensitivity is strongly improved, allowing the detection of CH_2O at concentrations as low as 80 ppb with a sensitivity of 2.6 $.10^{-3}$ $°.s^{-1}.ppm^{-1}$.

Nevertheless, figure 4(a) shows that the sensor suffers from a lack of selectivity toward humidity. Several characterizations of the sensors response under different relative humidity were carried out in order to determine the influence of this parameter on the sensors sensitivity. Figure 4(b) shows that under 10 %RH conditions, the sensitivity is divided by 7.5 in relation to dry conditions. Furthermore, the limit of detection increases to 100 ppb and 500 ppb respectively under 10 %RH and 20 %RH conditions while 80 ppb can be reached in dry conditions. The effect of adding a hydrophobic fluorinated chain in the formulation of the sensitive material is currently studied. We expect tat the improvement of this formulation will minimize the sensitivity to humidity and hence improve the selectivity of the sensor.

2) Carbon Monoxide Measurements: SAW delay line covered with new structures of corroles have been exposed to CO at low concentration. Figure 5(a) represents the sensor response to CO diluted in N_2 in the 10 ppm to 200 ppb range. This sensor has shown a great sensitivity to CO allowing the detection of concentration as low as 200 ppb. One can see a drift of the signal following the detection. This behavior is attributed to temperature changes when shifting from the carrier gas to the target gas. In order to address a response to that issue, a second delay line used as a temperature
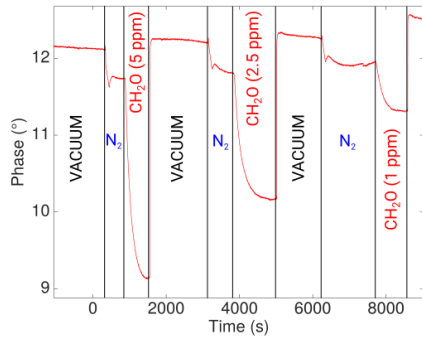
(a)
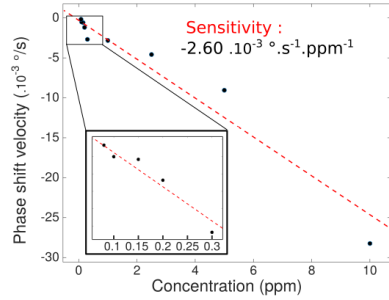
(b)

Fig. 3. (a) Measurements of CH_2O concentration with SAW devices functionalized with sensitive layer L2; (b) The correlation between the phase shift velocity during the exposure and the concentration of CH_2O
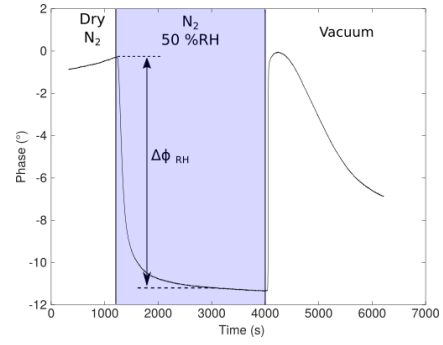

(a)

(b)

Fig. 4. (a) Measurements of CH_2O concentration with SAW devices functionalized with sensitive layer L2; (b) The correlation between the phase shift velocity during the exposure and the concentration of CH_2O

reference is currently under development. Figure 5(b) shows that despite of the temperature-related measurement problems, the signals observed are correlated to the CO concentration with a sensitivity of $1.32 \cdot 10^{-3} \,°.s^{-1}.ppm^{-1}$.
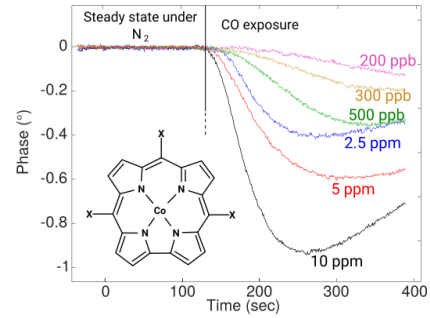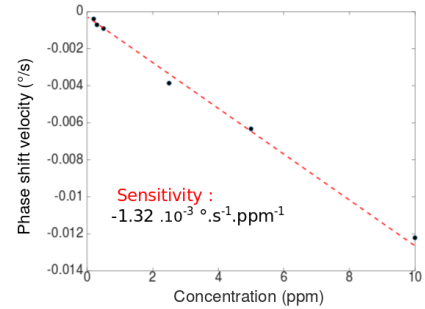
II. CONCLUSION

In this study, we have demonstrated a linear correlation between the phase velocity shifts of the Love wave and the concnetration of the target gases. The experiments were repeated several times to validate the results under various concentrations. We have shown that the use of Love wave devices functionalized with sensitive materials such as corrole complexes or nano-porous layers enables gas detection at concentrations as low as a few tens of ppb for CH_2O and a few hundreds of ppb in the case of CO. Besides the cross-sensitivity to humidity, these results pave the way to investigating other gas detection with specific functionalized acoustic waves devices.
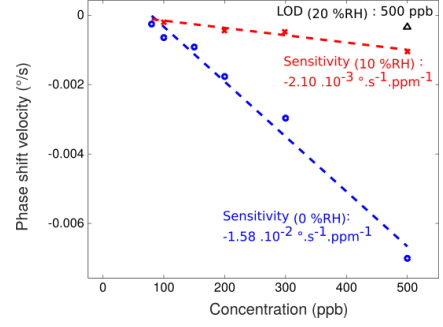
(a)

(b)

Fig. 5. (a) Phase signals of a functionalized SAW device to carbon monoxide in the 10 ppm to 200 ppb range; (b) Correlation between the phase shift velocity during the exposure and the concentration of carbon monoxide

REFERENCES

[1] W. Kim, N. Terada, T. Nomura, R. Takahashi, S. Lee, J. Park, and A. Konno, "Effect of formaldehyde on the expression of adhesion molecules in nasal microvascular endothelial cells: the role of formaldehyde in the pathogenesis of sick building syndrome," *Clinical & Experimental Allergy*, vol. 32, no. 2, pp. 287–295, 2002.

[2] J. A. Raub, M. Mathieu-Nolf, N. B. Hampson, and S. R. Thom, "Carbon monoxide poisoning a public health perspective," *Toxicology*, vol. 145, no. 1, pp. 1–14, 2000.

[3] World Health Organization (WHO) *et al.*, "WHO guidelines for indoor air quality: selected pollutants," no. 2010, 2010.

[4] A. Verrier, C. Ménard, P. Ardwison, C. Perrey, and J. Thiolet, "Caractéristiques socio-économiques des ménages accidentellement intoxiqués par le monoxyde de carbone (CO)," *Bull Epidémiol Hebd*, pp. 2–3, 2016.

[5] D. Rabus, J.-M. Friedt, S. Ballandras, G. Martin, E. Carry, and V. Blondeau-Patissier, "High-sensitivity open-loop electronics for gravimetric acoustic-wave-based sensors," *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*, vol. 60, no. 6, pp. 1219–1226, 2013.

[6] K. M. Kadish, Z. Ou, J. Shao, C. P. Gros, J.-M. Barbe, F. Jérôme, F. Bolze, F. Burdet, and R. Guilard, "Alkyl and aryl substituted corroles. 3. reactions of cofacial cobalt biscorroles and porphyrin-corroles with pyridine and carbon monoxide," *Inorganic chemistry*, vol. 41, no. 15, pp. 3990–4005, 2002.

[7] J.-M. Barbe, G. Canard, S. Brandès, F. Jérôme, G. Dubois, and R. Guilard, "Metallocorroles as sensing components for gas sensors: remarkable affinity and selectivity of cobalt (III) corroles for CO vs. O_2 and N_2," *Dalton Transactions*, no. 8, pp. 1208–1214, 2004.