Humidity Impact Reduction on WO_3 Gas Microsensor Response Using New Filters Based on Ionic Liquid

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***Abstract*— The detection of gaseous pollutants such as Benzene, Toluene, Ethylbenzene and Xylene (BTEX) under real conditions requires working in a humid environment. It is well known that the humidity reduces the performances of gas sensors, particularly in terms of sensitivity. Using a filter based on an ionic liquid (IL), low concentrations of BTEX can be detected with a tungsten trioxide (WO_3) thin film (50 nm) deposited by reactive radio frequency (RF) magnetron sputtering on a transducer which has developed in IM2NP laboratory. With this absorption upstream, we are able to detect 500 ppb of BTEX gases without a sensor sensitivity decrease with 50% relative humidity in the inlet feed.**

Keywords - gas sensor; humidity removal; tungsten trioxide; ionic liquid based filter.

I. INTRODUCTION

Air quality monitoring has become an important health and societal issue. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX gases) are among the targeted VOCs (Volatile Organic Compounds). It is well known that relative humidity is an important factor influencing the performance of metal oxide gas sensors, especially in terms of sensitivity [1]. In this work, we demonstrated the possibility to detect low BTEX concentration (500ppb) with 50% relative humidity in the inlet feed, without loss of the sensor sensitivity, using a WO_3 gas sensor with an ionic liquid (IL) based filter upstream. We also demonstrated that the ionic liquid only captures the humidity in air and does not affect the sensor response.

In Section II, we describe the WO_3 microsensor, the test bench and the IL filter. In Section III, we present and comment experimental results showing the effect of the IL filter on the detection of low BTEX concentration under 50% relative humidity.

II. MATERIAL AND METHODS

A. *Microsensor design and sensitive layer*

Our device is composed of an integrated Pt heater and Pt electrodes for the measurements, deposited by sputtering on a Si/SiO_2 substrate (Fig.1) [2]. The sensitive layer of tungsten trioxide (50 nm) was deposited on the top of these electrodes, by reactive RF magnetron sputtering. Then, the device was annealed at 723K during two hours in order to stabilize the crystallinity of the sensitive layer.

The tungsten trioxide (WO_3) is a n-type metal oxide with a large gap and oxygen vacancies. The conductivity of this oxide depends on the composition of the surrounding gas atmosphere [3].

During all our studies, we used an operating temperature of 513 K. The electrical measurements were made under a constant gas flow of 100 sccm.

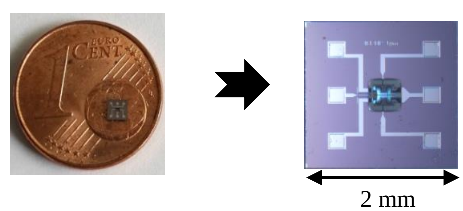

Figure 1. Design of the sensor device [2]

B. *Test bench for electrical characterization under BTEX gases and humidity*

We used a test bench specially designed for the BTEX detection in the presence of different humidity levels. It is composed of a gas dilution and humidification system that generates an output mixture at very low concentrations (1 to 500 ppb) with a variable humidity (0 to 90%), an integrated test cell and an acquisition system to characterize the electrical responses of the gas microsensor (Fig.2).

Humidity is generated starting from pressurized liquid water, which is vaporized through a microporous membrane. The water vapor is injected into the dry gas mixture by means of a proportional valve. This valve, controlled by a humidity

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sensor placed at the humidifier outlet, makes it possible to keep the hygrometry of the mixture constant. The vapor pressure is kept sufficient by heating and regulating the temperature of the vaporization cell. A second humidity sensor is placed at the output of the filter.

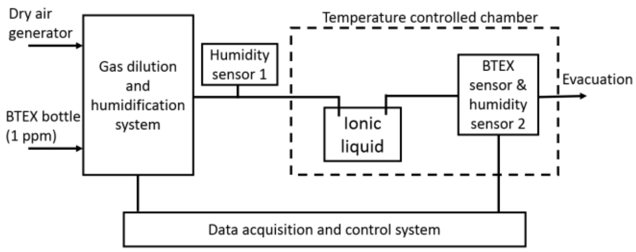

Figure 2. Diagram of the test bench.

C. Ionic liquid based filter

Ionic Liquids are classified like polar solvents and they have attractive properties such as low vapor pressure, thermal stability or selective solubility [4]. The innovation of this filter is to adsorb the water molecules in the atmosphere without capturing the BTEX gas molecules [5]. The 1-Butyl-3-methylimidazolium bromide (bmimBr) has been chosen for its great hygroscopic property. In order to eliminate the influence of a solid matrix or any other form of support, the filter is made by bubbling the gas mixture into a glass container filled with the IL.

III. RESULTS AND DISCUSSION

A. Influence of wet air on sensor response to BTEX

To study the humidity influence on the sensor response, we exposed our sensor to 500 ppb of BTEX for 4 minutes (Fig. 3) under dry air and wet air (50% RH). The sensor response was calculated using the relation (1):

$$Sensor\ response\ (\%) = \left(\frac{R_{air} - R_{gas}}{R_{gas}}\right) * 100 \qquad (1)$$

with R_{air}, the sensor resistance in air before gas exposure and R_{gas}, the sensor resistance in presence of BTEX.

Under dry air, the sensor response to 500 ppb of BTEX is 24%. The introduction of 50% of relative humidity in the atmosphere reduces the sensor response to 12%. The sensor response is divided by 2 under 50% of relative humidity.

This behavior is well known and has been already reported in the literature. Several hypotheses have been made about this behavior [6]. Firstly, the adsorption of the water molecules leads to a decrease in the chemical adsorption of the oxygen species on the surface of the metal oxide [7]. Secondly, The BTEX molecules compete with the water molecules to react on the same adsorption sites [8]. In both cases, the introduction of relative humidity in the atmosphere leads to a decrease of the sensor response.

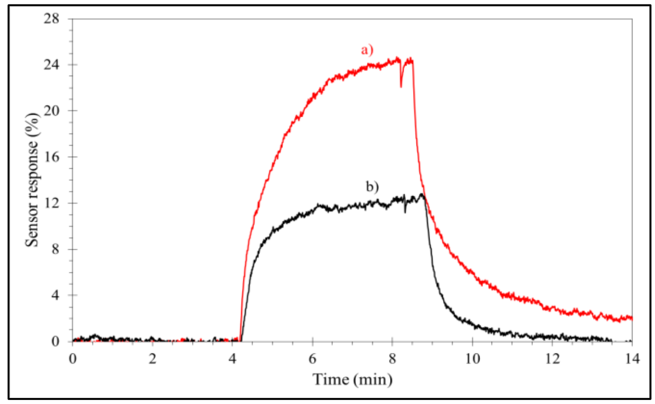

Figure 3. Sensors response under 500 ppb of BTEX, a) Dry air (0%), b) wet air (50%)

B. Influence of ionic liquid based filter on sensor response to BTEX under wet air

To reduce the humidity influence on the sensor response, we placed the IL filter upstream to the sensor and we exposed the sensor to 500 ppb of BTEX for 4 minutes (Fig. 4) under wet air (50% RH). In Figure 4, we can observe that when the IL filter is placed upstream the sensor, the response to 500 ppb of BTEX remains 25%. Hence, with this filter, we keep the BTEX detection performance of our sensor, even in presence of 50% of relative humidity in the atmosphere.

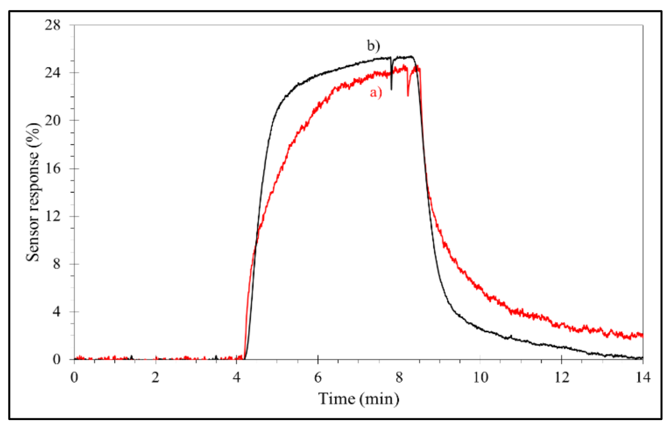

Figure 4. Sensors response under 500 ppb of BTEX, a) Dry air (0%), b) wet air (50%) with ionic liquid filter

The main objective of this work being to validate the filter ability to trap water vapor, we first chose to work with a 50% humidity rate which is considered as a good reference for gas sensors tests. Now that we have shown the performance of this type of filter, it will be interesting to study, in future experiments, the variation of operating conditions as higher humidity levels, different flow rate or BTEX concentration. This will help to understand at which humidity the sensor response significantly declines.

Furthermore, Figure 4 shows that the response of the BTEX sensor with the filter inserted into the gas flow is slightly higher and has a larger slope compared to the response under dry air. This behavior is reproducible. It may be related to the high viscosity of the ionic liquid, which causes pressure and flow rate variations at the gas sensor. Further experiments are needed to validate this hypothesis.

IV. CONCLUSION

In this work, we proposed a new solution to protect metal oxide gas sensors from the influence of humidity. We show the possibility to detect low BTEX concentrations under wet air with a WO_3 gas sensor associated with a filter based on an ionic liquid. We also demonstrated that the ionic liquid did not disturb the BTEX detection.

Further work is in progress to study the behavior of the IL filter under high humidity and to insert the IL into a solid matrix to make a more convenient filter [5].

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