Development of MOX Sensors for Low VOCs Concentrations Detection: Responses Comparison for WO_3, SnO_2, and ZnO Sensitive Layers with Interfering Gases as CO and CO_2

Short Paper

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***Abstract*—N-type Metal Oxide sensors was developed to detect Volatile Organic Compounds at low concentration level. Sensitive layers like SnO_2, ZnO and WO_3 were deposited by reactive RF sputtering method. The sensors is based on a heater and a MOX sensitive layer on a silicon substrate. Gas sensing properties have been investigated toward isobutylene, as a typical VOC and benzene. The optimum working temperature was experimentally determined at 285°C for this study. This work highlights the detection of VOCs with interfering gases by MOX sensor at low level. Gas like CO and CO_2 can be interfering gas for VOCs detection. This study was focused on the detection of isobutylene and benzene from 50 ppb to 500 ppb. The low selectivity is in fact a well-known problem of these sensors but we made a comparison between these MOX sensors at the same temperature in order to have a simple sensor array on the same chip in the future. This system will be used for a real time indoor air monitoring.**

Keywords- gas sensor; MOX sensor; isobutylene; benzene carbon dioxyde; carbone monoxyde.

I. INTRODUCTION

In the last decades, an increasing demand for the monitoring of several parameters allowing to guarantee the safety and quality products and environment represents a wide market for chemical sensors. Responses comparison between sensors allows to choose specific systems for a target gas [1]. In different fields, like environmental monitoring, home security, and safety, the detection and evaluation of gaseous emissions is strongly required [2].Volatile organic compounds (VOCs) are emitted to the atmosphere from various industrial and natural sources. The concentration of VOCs is much higher in indoors compared to outdoors, which not only pollutes the environment but also affects human health through breathing and skin contamination. VOCs are present in several household products such as paints, disinfectants, wood preservatives and automotive products. All these products contribute to indoor air pollution. There is a need to develop fast, sensitive, and cost-effective gas sensors for the detection of VOCs.

Gas sensing applications require continuous and direct exposition of gas sensors to environment to be analyzed with interferers. The most common gas sensing technology for sensing applications is metal oxide (MOX) gas sensors. The development of transducers for metal –oxide gas sensors has been reported lately [3].

MOX sensors in particular is still the most promising class of sensing materials, thanks to easy fabrication methods and chemical stability. In our case, MOX sensors are investigated in order to detect VOCs thanks to their miniaturization and real-time monitoring capabilities. These sensors need to be heated to elevated temperature to make them gas sensitive and to allow them to respond rapidly to the momentary gas concentration levels in the ambient air.

The sensitive layers have been obtained by Radio Frequency Magnetron Sputtering. Great attention was dedicated to the control of the film thickness. An appropriate choice of the materials for a particular gas is very important, and some materials are suitable for each type of gas detection. Considering that metal oxides are very good sensitive layer candidates, the analysis of various parameters including electro-physical properties and structural properties is important for the choice of an effective sensor. It is also necessary to pay attention to the performances towards interfering gases. An interesting approach to obtain enhanced selectivity consists in operating the sensors with variable temperature profiles or light modulation [4] [5]. Many different shapes and periods of the sensor temperature profiles have been proposed in the literature depending also on the particular structure of the sensors used [6]. Nevertheless, if different materials are on the same chip, the right choice have to be made in order to select the more sensitive layer for the gas at a working temperature.

Isobutylene, which is a typical VOC is one of our target gas because it is easy to detect. It is also easy to realize a concentration calibration with a photoionization detector for example. We will start with this gas then we will try to detect benzene which is more dangerous for human health. Benzene exposure can cause leukemia and permissible exposure limits have been set up. This two VOCs will help us to estimate how selective can be a system with our different sensors.

In this work, we have chosen three main n-type metal oxides used in this field: SnO_2 [7], WO_3 [8] [9], and ZnO [10]. The aim of the comparison between the performances of these sensitive materials is to find the best sensitive layer for our low VOCs concentrations sensors and to evaluate the effect of interfering gases like CO and CO_2. These interferences can be a problem when the detection system is too sensitive towards these gases.

II. SENSITIVE LAYER

A. *Deposition Method*

The three sensitive thin layers (~50nm) under study were deposited by reactive magnetron RF sputtering. So, the metal oxide films were grown by reactive R.F. magnetron sputtering of pure metal by means of a plasma of argon as carrier gas and oxygen as reactive gas. The experimental set-up was a conventional capacitive coupled R.F. magnetron sputtering chamber with a water-cooled cathode target. The deposition chamber was first pumped down to high vacuum conditions (10^{-7} mbar). Under a dynamic strangling pumping through a valve, pure oxygen was then introduced into the chamber and the partial pressure of oxygen was adjusted to the desired value (10^{-3} mbar) by means of a mass flow controller. Pure argon was afterwards introduced bringing the total working dynamic pressure up to 20 x 10^{-3} mbar. The R.F. forward input power was maintained at 100 W with a reflected power rendered minimum (almost zero) by means of an impedance matching. The corresponding self-bias voltage was around -100 V. These conditions were kept constant during the whole films depositions process. Only several parameters as the oxygen pressure and the deposition time were changed and studied to obtain the right oxide. Magnetron Sputtering is a low cost and easy control method for layer growth. Finally, the materials were annealed at 450°C during 1h30 to improve their nano-crystallization and the stability of the sensors response.

B. *Structural charatherizations*

X-ray diffraction (XRD) measurements were made using a Philips X'Pert MPD. The angular range was between 20° and 60° for 2θ. Data were collected with an angular step of 0.02°, 3 s per step. The Cu X-ray source was operated with a high intensity ceramic sealed tube (3 kW).

Fig. 1 shows the XRD patterns of the three thin film. All the diffraction peaks show tetragonal rutile structure for SnO_2, monoclinic structure for WO_3 and hexagonal structure for ZnO (JCPDS cards No 72-1147, 41-1445, 36-1451 respectively). The grains size of these materials was around 20 nm for each one high porosity (Fig. 2).

Under isobutylene, the reducing molecules will react with the adsorbed oxygen ions and release the trapped electrons back to the metal oxide conduction band. This reaction leads to the decrease of electron depletion barrier and to increase the electrical conduction of the metal oxide. The same reaction happened under benzene.

The sensitive layer is the main part of the gas sensor. The right choice have to be made about this material in order to obtain the best response possible. All these materials have to be studied for each VOCs.

The material characterization was also carried out by using scanning electron microscopy (SEM). A SEM image of one the SnO2 film is shown in Fig. 2 to appreciate the morphology. All these materials shown the same surface properties that have helped us to compare them.

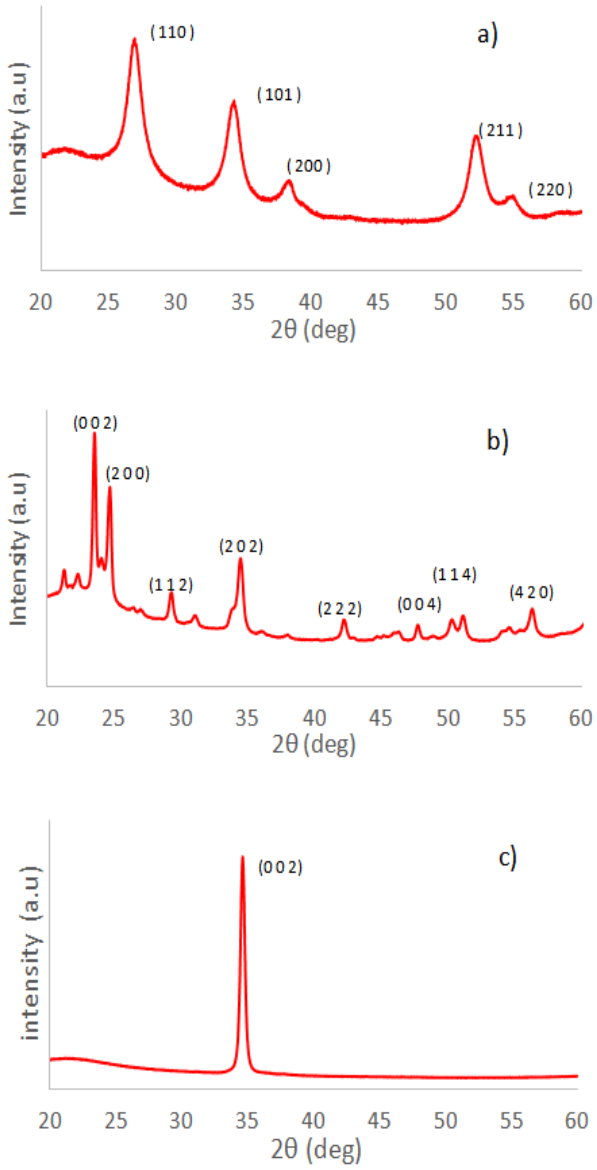

Figure 1. XRD patterns of a) SnO_2, b)WO_3 and c) ZnO made by reactive RF sputtering

The material characterization was also carried out by using scanning electron microscopy (SEM). A SEM image of one the SnO_2 film is shown in Fig. 2 to appreciate the morphology. All these materials shown the same surface properties that have helped us to compare them. The grain size was around 20 nm, with homogeneous shapes.

These layers are the main part of the detection system and their structural characterization was decisive to identify them and understand their behavior under gases. We looked for a simple deposit method and characterization methods to demonstrate the feasibility of the process on an industrial scale.

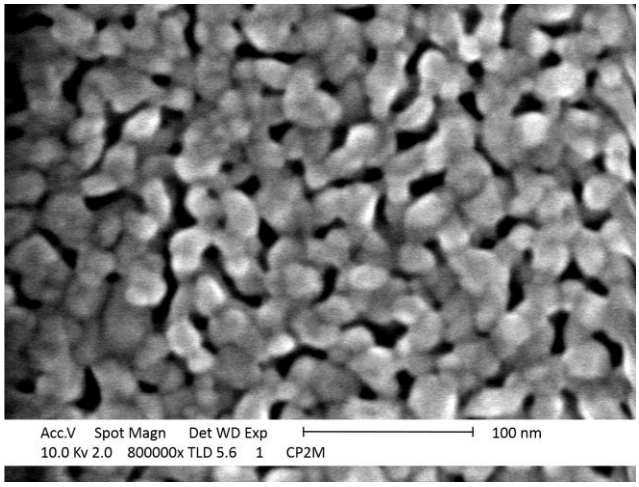

Figure 2. SEM of a SnO_2, layer

C. Chip gas sensor

The gas sensors fabricated with SnO_2, WO_3 and ZnO layers as sensitive material is presented in Fig. 3. It was made of Si/SiO_2 substrate with Ti/Pt interdigitated electrodes. The sensitive layer was deposited on and between the electrodes by reactive magnetron RF sputtering. These materials were the sensitive layers which will interact with isobutylene in this case. This chip was on a hotplate that allowed us to reach temperature of 285°C. The temperature was monitoring thanks to a K type thermocouple.

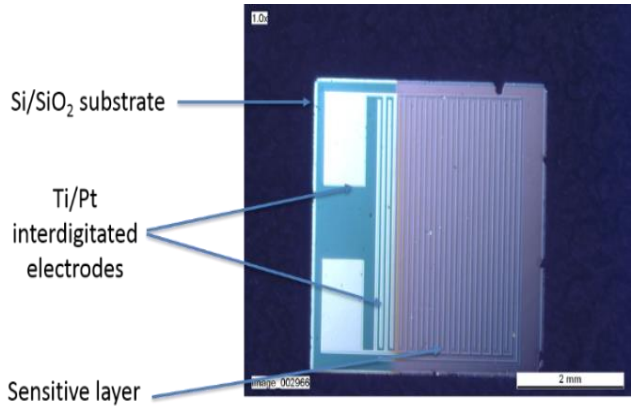

Figure 3. MOX Sensor with Si/SiO_2 substrate

So, three sensors with the different layers were made to obtain the same thickness and the same grain size. These sensors were made with the same conditions in order to elaborate them on the same chip in the future, for a sensors array. This is the first version of the chip. The final device could have the three materials on the same chip at the same temperature. Particular attention should be given on the test conditions to realize the comparison between the sensors.

III. METHODS

A. Gas test bench

This device has been tested with an automated gas bench (Fig. 4) with isobutylene, benzene, carbon monoxide and dioxide. We used a power supply to control the operating temperature and a source meter for the data acquisition. This target gas was injected into a dilution system with or without interfering compounds. The outline was connected to a thermo-regulated test chamber. For each concentration, the sensor was exposed to gas for 1 min then to dry air during 10 min. The sensors were maintained at the nominal heating voltage in dry air until the baseline was obtained to reach the response [11] under a flow rate of 500 sccm.

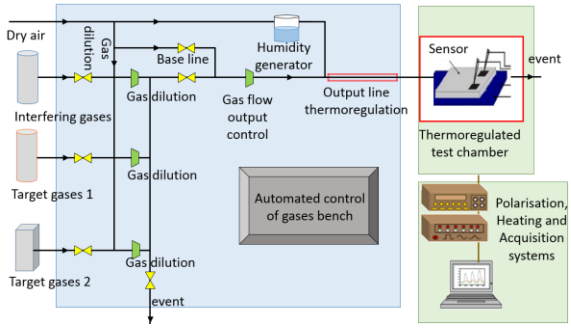

Figure 4. Gas measurement experiment set-up

The device electrical resistance was recorded by forcing 0.1 V as the polarisation using a Keithley system. We had measured the current I to obtain the polarization resistance. The data acquisition is controlled by a PC via a Labview program and stored for futher analysis.

The target gas includes two VOCs including isobutylene and benzene, and two interfering gases as carbon monoxyde and dioxyde. All of them are reducing gases diluted in synthetic air at different concentrations with a constant total flow of 500 sccm. These devices have been tested at room temperature.

B. Tested vapours

Isobutylene is a typical VOCs, currently used for concentration calibration. We also used calibrated concentrations of benzene by using a permeation tube. All the concentration were checked with a photoionization detector. The outline was heated to prevent a gas condensation and it was connected to a thermo-regulated test chamber. The test were realized without humidity in order to characterize the influence of the interfering gases alone at stationarity temperature regime.

IV. RESULTS

A. Response to isobutylene

Many authors have characterized oxygen adsorption state on metal oxide and discovered four species: O_2, O^{2-}, O^- and O_2.

The oxidation of isobutylene on the oxide surface can lead to a change of the resistance material. When this reducing gas is oxidized by the oxygen ions on the metal oxide surface, an electron is given back to the oxide. Then the resistance of the gas sensor decreases.

Fig 5 shows a typical responses with a wide range of detection from 50 ppb to 500 ppb of isobutylene at 285°C. WO_3 and ZnO sensors seem to be the best devices for isobutylene. We have reached the highest responses from the three sensitive layers with low concentrations.

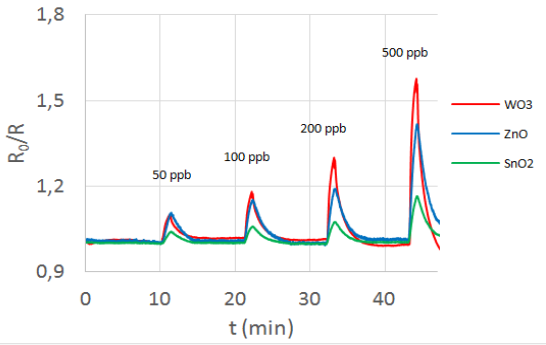

Figure 5. Sensors response for isobutylène concentrations, from 50 ppb to 500 ppb.

These results show fast response to isobutylene at 285°C. We reached a response of 1.6 with WO_3 although we reached 1.15 with SnO_2. These two results will allow us to have a specific response for isobutylene from our system.

B. *Response to benzene*

The oxidation of benzene on oxide surface can also lead to the generation of electrons .Fig. 6 shows lower responses for benzene than isobutylene with the range of detection from 50 ppb to 500 ppb of isobutylene. The working temperature was the same as the previous test.

ZnO and SnO_2 sensors are the best devices for benzene. We can noticed that the WO_3 sensor has the worst response for this gas. So, we will be able to compare the responses for each VOCs and improve the selectivity of our future system with three sensors.

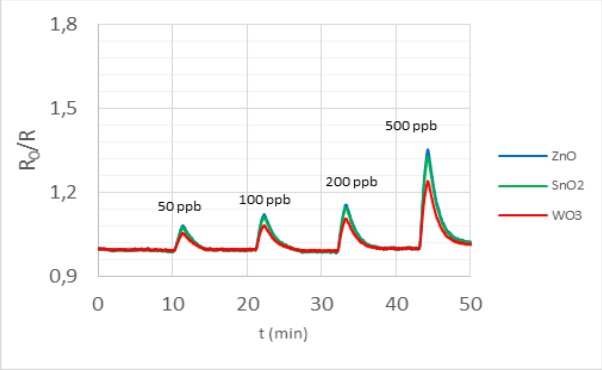

Figure 6. Sensors response for benzene concentrations, from 50 ppb to 500 ppb.

C. *Influence of interfering gases*

We have chosen 10 ppm of CO and 1% CO_2 as interfering gases concentrations. These are the type of concentration we can meet in ambient air. The Fig. 7 shows the comparison of the responses of the three materials and for the two gases.

Sensors were exposed to this interfering concentration with the same conditions as isobutylene i.e., 1 min exposition time then 10 min of dry air at 500 sccm.

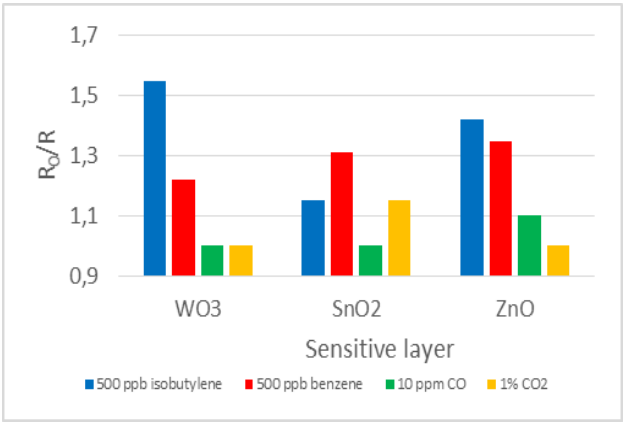

Figure 7. Sensor response under isobutylene and interferring gases

WO_3 and SnO_2 show low responses towards CO and CO_2 despite the better response for the target gases. With tests under the same experimental conditions (Fig. 7) we can classify the right metal oxide for a target gas like isobutylene in presence of interfering gases.

A system based on metal oxide gas sensor array [12] [13] and pattern recognition algorithms could give an identification for each gas according to the sensors response. The temperature modulation could also help to obtain better selectivity.

V. CONCLUSION

A set of sensors of single metal oxide has been selected to detect isobutylene and benzene. An array of sensors was then obtained at the same temperature. In the background of realistic concentrations of CO and CO_2 showed high selectivity to VOCs.

According to these results, the gas measurement showed fast response / recovery times towards isobutylene and benzene. The best sensitive layers are WO_3 and ZnO for isobutylene because we have the highest responses for this gas and the weakest influence towards gases like CO and CO_2. The best sensors for benzene are ZnO and SnO_2 for the same reasons. This is the first step for air gas monitoring. We want to improve the selectivity towards others VOCs. On the other hand, and after identifying the appropriate sensitive materials, we plan to study the improvement of the selectivity of these sensors. This array could be being used with test procedure applied to an isotherm mode. Also, this study can be the beginning of a study of detection of VOCs with three sensitive materials on the same chip.

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