Development of metal oxide gas sensors for very low concentration (ppb) of BTEX vapors

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Abstract. The control and analysis of air quality have become a major preoccupation of the last twenty years. In 2008, the European Union has introduced a Directive (2008/50/EC) to impose measurement obligations and thresholds to not exceed for some pollutants, including BTEX gases, in view of their adverse effects on the health. In this paper, we show the ability to detect very low concentrations of BTEX using a gas microsensor based on metal oxide thin-film. A test bench able to generate very low vapors concentrations has been achieved and fully automated. Thin metal oxides layers have been realized by reactive magnetron sputtering. The sensitive layers are functionalized with gold nanoparticles by thermal evaporation technique. Our sensors have been tested on a wide range of concentrations of BTEX (5 - 500 ppb) and have been able to detect concentrations of a few ppb for operating temperatures below 593 K. These results are very promising for detection of very low BTEX concentration for indoor as well as outdoor application. We showed that the addition of gold nanoparticles on the sensitive layers decreases the sensors operating temperature and increases the response to BTEX gas. The best results are obtained with a sensitive layer based on ZnO.

1. Introduction

Monitoring and analysis of the outdoor air quality has become a major concern of the past 20 years. Several toxicological and epidemiological studies have shown that air pollution causes respiratory problems, asthma, cardiovascular disease and cancer. Air pollution is estimated to be responsible for more than 300,000 premature deaths in the Europe per year [1] [2]. Since 2008, the European Directive 2008/50/EC imposes concentration thresholds for some pollutants as BTEX gas (Benzene, Toluene, Ethylbenzene and Xylene) on a european scale. Many researches have been done to meet the requirements of new european standards for regulating the air quality and many research teams have looked at sensors based on metal oxide for the detection of volatile organic compounds (VOCs) as BTEX.

Several metal oxides have been reported in the literature for the detection of Benzene and Toluene. D. Ghaddab and Al. [3] studied the zinc oxide for its responsiveness to BTEX gas. Tungsten oxide also shows interesting performances in the presence of BTEX and this oxide is less affected by humidity variations. K. Kanda and Al. [4] were able to detect concentrations of 100 ppb of BTEX to 693 K with a sensitive layer of WO\textsubscript{3} of 35 µm of thickness. Moreover, W. Tang and Al. [5] showed a clear improvement in performance of sensitive layers by a "surface doping" with noble metals such as platinum and gold. The addition of noble metals on the surface would reduce the potential barriers and modify areas of space charge of the metal oxides according to a study by F. Li and Al. [6]. Furthermore, it would decrease the activation energies required for the creation of bonds to the surface of the sensitive material. Thus, it facilitates physical and
chemical reactions between the compounds studied and metal oxides and improves the performances of the sensors.

In this paper, we will demonstrate that our sensors can detect BTEX concentrations of 5 ppb at temperatures below 593 K, using metal oxide layers produced by reactive magnetron sputtering.

2. Experimental

WO₃ and ZnO thin films were prepared by reactive radio frequency (13.56 MHz) magnetron sputtering using 99.99% pure tungsten and zinc targets. The vacuum chamber was evacuated to $5 \times 10^{-10}$ bar by a turbo molecular pump. The films were sputtered on SiO₂/Si substrates with platinum (Pt) electrodes, in a reactive atmosphere under different oxygen–argon mixtures. The films thickness are about 50 nm. Both argon and oxygen flow were controlled by mass flow controllers. The total gas flow was maintained constant at 10 sccm, keeping the total pressure in the deposition chamber at 3 mbar. Oxygen content in the gas mixture during the layers’ realization, defined as the ratio of oxygen flow to the total flow, is fixed at 50% for WO₃ and at 40% for ZnO. As WO₃ and ZnO layers are highly resistive, interdigitated electrodes were used in order to reduce the sensor resistance. The distance between the electrodes was 50 µm. They were obtained from a sputtered Platine (Pt) film, using photolithography and lift off processes. After the sensitive layer’s deposition on the Pt electrodes, the films were annealed at 743 K for 90 minutes in air in order to stabilize the chemical composition and the crystalline structure. The addition of gold particles was performed by thermal evaporation technique.

The samples were kept in dry air and no conditioning step was carried out before the sensor characterizations.

Bragg–Brentano (0–2θ) X-ray diffraction (XRD Philips XPERT MPD) was applied to check the crystallinity and the structure of the films. CuKα radiations ($\lambda = 0.154$ Å) with a scanning rate of 1°/min were used for the XRD analysis.

To investigate the BTEX sensing properties of WO₃ and ZnO thin films, we designed a measurement system for obtaining gas concentrations from 1 to 500 ppb with control of the relative humidity inside the test chamber. The measuring bench consists of several elements:

- A system of gas dilution and humidification that generates an output mix at very low concentrations of 1 to 500 ppb with a variable humidity (0 to 90%) and an adjustable output rate between 10 and 500 sccm.
- An integrated test cell made in our laboratory to characterize the electrical responses of the sensors in the presence of gas mixture in terms of sensitivity, speed, repeatability.
- An acquisition system that measures the electrical responses of three sensors simultaneously. It consists of three sourcemeters (Keithley 2450) and a programmable power supply (Rhodes & Schwarz HMP4040). The data were collected on a PC through GPIB interface. The programs interface allowing the control of the measuring devices and the signal acquisition have been developed under "LabVIEW Software".

3. Results and discussion

3.1. ZnO and WO₃ thin film structure

The results obtained by X-ray diffraction show diffraction peaks corresponding to WO₃ with a monoclinic structure P21/n and the polycrystalline ZnO films have a preferential growth parallel to the plane (002), which corresponds to the Wurtzite structure. We used Scherrer formula to calculate the size of crystallites (D). The crystallite size in the sensitive layers of ZnO and WO₃ are 15 nm and 10 nm respectively.

3.2. Sensing properties

One of important parameters of the MOX sensor sensibility is the temperature of the sensitive layer. This behavior can be explained by considering the temperature dependence of the surface coverage of chemisorbed species. At low temperature, the desorption phenomenon is weak and a total coverage of the sites can be obtained easily by ambient oxygen making any reversible detection impossible. Conversely, at
high temperature the efficiency of the desorption mechanism increases and the system will be less sensitive. There is thus necessarily an optimum temperature at which the sensor has a maximum of sensitivity.

The sensor response was defined as \( \frac{R_{\text{air}}}{R_{\text{gas}}} \), where \( R_{\text{air}} \) and \( R_{\text{gas}} \) are the resistance of the sensor in air and in tested gas, respectively. In order to check the effect of working temperature on the sensors response, sensors were maintained at various temperatures from 493 to 593 K.

The figure 1 illustrates the response to 500 ppb BTEX versus working temperature. In the case of \( \text{WO}_3 \), the best response \( \frac{R_{\text{air}}}{R_{\text{gas}}} = 2.45 \) is obtained for an optimum temperature of 533 K. For \( \text{ZnO} \), the best response \( \frac{R_{\text{air}}}{R_{\text{gas}}} = 2.95 \) is reached at 573 K. The addition of gold nanoparticles on the surface of the sensitive layers have very significant effects on BTEX detection properties.

Indeed, the temperature decreases for both metal oxides films studied with the addition of gold nanoparticles and the response is greatly improved. For the case of the sensitive layer of \( \text{WO}_3 \), it improves the response to BTEX from 2.45 to 3.25 with a decreasing of the optimum temperature from 533 K to 493 K. For \( \text{ZnO} \), we can observe the same phenomenon. The response of the modified \( \text{ZnO} \) with gold is 4 at 533 K against 2.95 at 573 K for the pristine \( \text{ZnO} \).

This study also allowed us to determine the response times and recovery times of the studied metal oxides. The addition of gold nanoparticles also decreases the response times and the recovery times. The addition of gold nanoparticles on the surface of metal oxide improve of the sensitivity of the sensor by means of selective reaction of a desired molecule in a selected site.

P. Montmeat and Al. [7] explain this mechanism of improvement of the sensitivity. The reaction of molecules of target gas takes place on the surface of the additives and not the surface of the substrate. These additives change their state of charge, which results in a variation in the height of the potential barrier, which leads to a conductance change on the metal oxide. Furthermore, the addition of gold nanoparticles as active catalyst creates active sites that are considered essential for the improvement of sensitivity obtained on the sensitive layers tested. These hypotheses are in agreement with our results presented in table 1.

In order to investigate the detection limit of our sensors, we submitted our sensitive layers to different concentrations of BTEX between 5 and 50 ppb. The results obtained are shown in figure 2.

![Figure 1. Sensors response vs temperature in presence of 500 ppb of BTEX.](image1)

![Figure 2. (a) Response of the four studied sensors at different temperature in presence of BTEX, (b) Resistance of Au-ZnO at 533 K for different concentration of BTEX.](image2)
4. Conclusion
We realized BTEX sensors by reactive magnetron sputtering. The sensitive layers have been optimized to detect low concentration of BTEX gas. The thin film of ZnO and WO₃ are capable of detecting concentrations of 5 ppb of BTEX vapors. The addition of gold nanoparticles on the surface of the thin film improves the response to BTEX and the response/recovery time. Besides, it decreases the operating temperature of the sensing layer. The best results have been obtained with a thin layer of ZnO doped with gold nanoparticles on the surface and they are very promising for the realization of sensor for the control of the air quality.

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| Material  | Concentration (ppb) | Response (R<sub>all</sub>/R<sub>gas</sub>) | Temperature (K) | Reference |
|-----------|---------------------|------------------------------------------|-----------------|-----------|
| WO₃       | 500                 | 2.65                                     | 693             | [5]       |
| ZnO       | 500                 | 1.2                                      | 493             | [3]       |
| SnO₂/VO₃  | 80                  | 1.58                                     | 543             | [9]       |
| TiO₂      | 100                 | 1.25                                     | 368             | [6]       |
| WO₃       | 5                   | 1.02                                     | 533             |          |
| ZnO       | 5                   | 1.075                                    | 573             | This work |
| Au-WO₃    | 5                   | 1.16                                     | 493             | This work |
| Au-ZnO    | 5                   | 1.28                                     | 533             | This work |

Table 2. Summary of results reported in the literature