Metal oxide-based gas sensor and microwave broad-band measurements: an innovative approach to gas sensing

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Abstract. We outline the development of a gas sensor using microwave technology (0.3 MHz to 3 GHz). The sensor is a coaxial structure into which is introduced a sensitive material. An electromagnetic field (microwave), sent out through the sensor by a vectorial network analyzer, solicits the sensitive material exposed to a gas. The observed variation in the sensor response is due to the variation in the adsorption of this gas. SrTiO$_3$, demonstrated to be the highly sensitive to water vapour, is exposed to different gases (saturated vapour of water, ethanol and toluene). The response of the sensor is quantitative and typical for each gas. This method of measurement leads to the development of an alternative to the current gas sensor.

1. State of the art in the field of gas sensing
There is a great demand to enhance the sensitivity of chemical sensors for applications such as monitoring and control of air quality, detection of flammable or toxic gases, medical diagnosis, detection of chemical-warfare agents, and optimization of combustion efficiency in automobile engines. It must be emphasized that three broad categories of gaseous species are concerned: toxic species (CO, SO$_2$, NO$_x$, COV...), corrosive species (Cl$_2$, F$_2$, HF...) and explosive species (CH$_4$, hydrocarbons, nitrous compounds ...). The first category is essentially monitored in cities and homes. The second is associated with industry (chemical, petrochemical and food industries), whereas the third essentially concerns public security.

An abundant literature describes gas-sensing technologies and their mechanisms as well as the evaluation of gas concentrations. The techniques will be grouped into two categories: direct and indirect measurements.

1.1. Direct and indirect measurements
Direct measurements regroup different technologies. Chromatographs and different spectrometers allow for the quantitative determination of gas concentrations [1, 2, 3]. The IR tunable diode laser absorption spectrometer [4, 5, 6] or the millimeter wave (MMW) spectrometer [7, 8] can be used to determine atmospheric trace gas constituents. Pushkarsky et al. [9] also reports high sensitivity detection of chemical warfare agents with laser photoacoustic spectroscopy. Finally, Zhu uses a microwave spectrometer with a resonant cavity gas cell to determine concentrations
of ethylene oxide gas [10]. Although a large number of publications report good gas sensing performance, these techniques are essentially used in the laboratory because of their cost, their volume or their complexity.

Indirect measurement principally refers to portable sensors which are based on the interaction between the studied gas and a sensitive material. Among the most common of such gas sensors are: piezoelectric quartz crystal (PQC) [11] and surface acoustic wave (SAW) oscillators [12, 13], solid state gas sensors based on solid-electrolytes [14], on catalytic combustion [15] or on electronic property modulation of semiconducting oxides [16, 17, 18, 19]. In recent years, field effect transistors (FET) have been developed [20, 21]. Microwave resonant sensors (microstrip structure) [22, 23] and sensors based on impedance spectroscopy at low frequency [24, 25, 26] have also been discussed. However, over 1 GHz, only resonant circuit [22, 23] and nonresonant waveguide [10] have been used to determine the concentration of a gas.

1.2. Metal oxide as sensitive material
Metal oxides are the subject of extensive investigations, particularly SnO$_2$ [27]. In more recent research, interest has shifted to other promising metal oxides (In$_2$O$_3$ [28], SrTiO$_3$ [24], WO$_3$ [29], ZnO [30]), or multicomponent metal oxides (CuO-ZnO [31], nickel ferrite [32], TiO$_2$-WO$_3$ [33]). Certain other materials, such as polysulfone [26], are also used.

Metal oxide gas-sensing materials are selected according to their gas-sensing properties: selectivity, sensitivity, response time, etc. Eranna et al. have reviewed different metal oxides used in the development of different integrated gas sensors [34]. The gas-sensing mechanism with metal oxide materials is based on the adsorption and the reaction between the surface of the materials and the gas molecules. This mechanism depends upon the microstructure of the materials, namely, specific area, particle size and porosity, as well as on the thickness of the sensing film, on its adaptability to a wide variety of reductive or oxidative gases, on its thermal stability and on its ability to produce high reproducibility. Gas sensing techniques using metal oxides rely on changes in d.c. conductivity due to adsorption of polar chemicals. Device sensitivity depends on the magnitude of d.c. conductivity change before and after adsorption. Enhancement of device sensitivity can be obtained by operating at high temperatures (200-600 °C). These operating conditions achieve interaction between semiconducting metal oxides and the gas molecules to be detected. However, slight selectivity between different kinds of gases is frequently observed.

1.3. A new approach: microwave broadband measurements and metal oxide
A new direction in gas sensing is proposed here. Microwave broadband measurements (300 kHz-3 GHz) are taken using a homemade coaxial sensor. Conductivity decreases strongly with frequency and may be negligible within the microwave domain. However, gas adsorption can induce strong changes in dielectric properties within a specific frequency domain in strong relationship with the chemical nature of gases and metal oxides. The reflection coefficient of the sensor represents these dielectric property changes. The aim of this study is to assess this new gas sensing technique. The sensitive material is subjected to a microwave solicitation. In the presence of a gas, the dielectric properties of the sensitive material vary extensively in the microwave frequency range, which is not the case in the low frequency range [24].

2. Nature and principle of the microwave gas sensor system
The experimental configuration to test the sensor consists of a test chamber connected to a vacuum pump and a gas chamber, and a HP8752A vectorial network analyzer linked to a GPIB
data acquisition system. A hermetic SMA-N adaptor is inserted into the test chamber and is connected to the vectorial network analyzer. The SMA-N is a microwave propagation structure and is composed of a outer conductor a central core separated by an isolator. The sensitive material is introduced into this coaxial structure and replaces the isolator. The design of our sensor assures thus electromagnetic propagation in the sensitive material [35]. The frequency response is specific to the geometry of the sensor, to the dielectric properties of the sensitive material as well as to their variation in the presence of a gas.

The experimental process is carefully respected. A vacuum is established in the cell before each measurement. The measurements are carried out sequentially while decreasing the pressure from 60 to 10 mbar. Data acquisitions are executed 1 and 5 minutes after pressure stabilization.

The vectorial network analyzer carries out the measurements in the frequency range (300 kHz-3 GHz). The obtained values consist of an input reflection coefficient $\Gamma$ or $S_{11}$, a complex number. Therefore, the variation of the reflection coefficient leads to a variation not only in its real part but also in its imaginary part. In order to compare the responses of different materials, a variable is defined by [36]:

$$\text{Sensor response : } \frac{\Delta \Gamma}{\Gamma} = \frac{\Gamma_{\text{gas}} - \Gamma_{\text{vacuum}}}{\Gamma_{\text{vacuum}}}$$

where $\Gamma_{\text{vacuum}}$ and $\Gamma_{\text{gas}}$ are the reflection coefficients before and after introduction of the gas, respectively.

In addition, at each frequency, the reflection coefficient provides two data describing the interaction between the gas sensor and the gas. In our case, 201 frequencies are used therefore 402 elements of data on the interaction between the gas and the sensor are obtained.

3. Sensor response versus time or frequency

In order to check the influence of the sensitive material on the sensor response, a series of experiments is performed with and without sensitive material. In both cases, the sensor is exposed to a normalized saturated water vapour pressure for two hours.
Figure 1 shows the time evolution of the reflection coefficient (imaginary part) associated with the sensor in both cases. The selected frequencies are 500 MHz, 1 GHz and 3 GHz. The interaction between the sensitive material and the gas is clearly demonstrated and excludes all other explanations of the variation in the sensor response.

The frequency evolution of the imaginary part of $\Delta \Gamma / \Gamma$ at different saturated water vapour pressures is given in figure 2. The sensitive material used is a zeolite 4A. In the frequency range of impedance spectrometry (below 1 GHz), the reflection coefficient $\Delta \Gamma / \Gamma$ indicates weak variation for each water pressure. Above 1 GHz, the variation of $\Delta \Gamma / \Gamma$ with water pressure is clearly distinguishable in comparison with the error dispersion (0.01%).

4. Sensor response versus the choice of sensitive material and/or gas
The sensitivity of the process with saturated water vapour is evaluated using different sensitive materials studied in the literature: zeolite 4A, SnO$_2$, SrTiO$_3$, TiO$_2$, ZnSO$_4$, and ZrO$_2$.

The frequency is fixed at 2 GHz and the water pressure is normalized. Table 1 presents the

| Sensitive material | Real part of $\Delta \Gamma / \Gamma$ (± 0.01%) | Imaginary part of $\Delta \Gamma / \Gamma$ (± 0.01%) |
|--------------------|---------------------------------------------|-----------------------------------------------|
| Zeolite            | 0.62                                        | 2.09                                          |
| SnO$_2$            | 0.02                                        | 0.15                                          |
| SrTiO$_3$          | 1.31                                        | 13.72                                         |
| TiO$_2$            | 0.06                                        | 0.01                                          |
| ZnSO$_4$           | 0.16                                        | 0.21                                          |
| ZrO$_2$            | 0.06                                        | 0.39                                          |
real and imaginary parts of $\Delta \Gamma$ according to the different sensitive materials. The variations in the imaginary part are superior to the variations in the real part of $\Delta \Gamma$. The optimal value of the imaginary part of $\Delta \Gamma$ is obtained using SrTiO$_3$ (13.72%), whereas the common sensitive material SnO$_2$ gives mediocre results (0.15%). SrTiO$_3$ therefore seems to be the most sensitive material in terms of detection of saturated water vapour.

The selectivity of the sensor containing SrTiO$_3$ is tested with a saturated vapour of ethanol, toluene and water. For purposes of comparison, the results are presented in two graphs: the real part of $\Delta \Gamma$ on the left and the imaginary part of $\Delta \Gamma$ on the right of figure 3, both at 2 GHz. For each gas, specific responses are clearly visible (real part and imaginary part). The evolution of $\Delta \Gamma$ of SrTiO$_3$ at 2 GHz underlines a direct relationship between the imaginary part and the saturated water vapour pressure. At the present time, many tests are being performed to confirm that this gas sensor effectively distinguishes between different gases.

To interpret these results, it is necessary to recall some facts. Gas sensors are based on the adsorption/desorption or chemical reactions on the surface of the sensor material. These reactions lead to physical changes, which are detected by the sensor device. In our case, the physical change observed is the variation of the reflection coefficient of the sensor. As mentioned above, the response is specific to the geometry of the sensor, the dielectric properties of the sensitive material, and the interaction sensitive material/gas. However, the variation in the reflection coefficient is strictly due to the interaction material/gas measured at different frequencies. An equivalent approach using a conductimetric gas sensor could be developed in order to explain the chemico-physical phenomenon inside the sensitive material. Further work is necessary to develop a numerical model to describe this phenomenon. Future work will also include the development of a relationship between the gas concentration and the permittivity of the sensitive material.

5. Conclusion
The present work reports on the capacities of a microwave gas sensor composed of a coaxial structure into which sensitive material is introduced. Using a vectorial network analyzer, the variations in the reflection coefficients of different metal oxides subjected to a gas are measured. The adsorption of gas molecules onto the sensitive materials tested is the fundamental mechanism that induces change in the reflection coefficient. The most significant results are obtained...
with SrTiO$_3$ and indicate a high sensitivity and selectivity to different gases. Indeed, reflection coefficient values are different for water, ethanol and toluene. More investigation will be undertaken in order to increase its sensitivity. Nevertheless, the promising results presented in this paper underline the originality of this technique which constitutes an interesting alternative to the current gas sensor.

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