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Microwave signature for gas sensing: 2005 to present

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ABSTRACT

We present here the development and the implementation of a technique of gas detection involving a microwave transduction method. The use of low-cost sensors based on microstrip or coplanar structures, adapted to the microwaves domain, allows the sensitive materials deposition under various forms. The purpose of the study is to assess the interest of microwave transduction for gas detection. The choice of the sensitive materials concerns materials widely used in the field of gas sensing: the metal oxides (SnO_2 and TiO_2) as well as molecular materials like cobalt phthalocyanine (CoPc). In this article we shall apply to explain the principles of the microwave transduction before approaching the conception of the sensors, the measurement protocols and the analysis obtained in various situations of measurement.

1. Introduction

The gas detection is a subject of study more and more tackled in connection with environmental and health safety problems (Yamazoe and Miura, 1994; Zhou et al., 2014; Donga et al., 2010). Whether

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for the control of industrial emissions (Soldan et al., 2014) or indoor quality air supervision (Suriano et al., 2014; Amodio et al., 2014), the challenge remains to produce detection systems with weak production and use costs, of high performance (sensitive, selective, reliable) and adapted to atmospheric conditions (linked to detection scales fixed by environmental standards). Qualitative and quantitative analysis of gaseous compounds such as VOC, NH_3, CO_2, CO, O_2, O_3 or H_2 are performed by operating very various sensitive materials (organic materials (Rossignol et al., 2013; Itagaki et al., 2005; Bouvet et al., 2013; Trometer et al., 1992), metal oxides (Korotcenkov, 2014; Jouhannaud et al., 2008; Barsan et al., 2007; Jiménez-Cadena et al., 2007)) and transduction techniques among which we can quote methods based on electrical (Jiménez-Cadena et al., 2007; Airoudj, 2007), optical (Jiménez-Cadena et al., 2007; Airoudj, 2007; Lim et al., 2011), acoustic (Jiménez-Cadena et al., 2007; Airoudj, 2007; Shapira et al., 1976), spectroscopic (Jiménez-Cadena et al., 2007; Airoudj, 2007) or calorimetric (Jiménez-Cadena et al., 2007; Airoudj, 2007) variations.

In any case, the gas sensing mechanism can be described as an adsorption/desorption process. Thus, one of the key element of a gas sensor is its sensitive material. The interaction between a gas and a sensitive material can be depicted according to: chemisorption (Gomri et al., 2005; Calvini and Levi, 2005), physisorption (Levi and Pisoni, 2004; Barochi et al., 2011), or both. In the case of chemisorption, an atomic connection is created by the interaction between the gas and the material, modifying the material characteristics in an irreversible way. To desorb the gas from the material, and thus eliminate formed bounds, an energy supply must be applied to the material through a heating. In the case of a physisorption, the interaction causes disturbances, modifying temporarily the material characteristics. The main interactions involved are Coulomb and Van Der Waals forces. As no atomic bounds are constituted, the modifications of the material characteristics are temporary. The sensitive material does not need any energy supply to regain its initial characteristics.

Most of the commercialized gas sensors are based on conductimetric transduction using non-stoichiometric metal oxides as sensitive materials (Gurlo, 2006). They present a long lifespan with a ppm resolution and response times compatible with environmental standards at low-costs. They are mainly sensitive to redox active species which can accept or give electrons, inducing a variation of the charge carriers density (Jouhannaud et al., 2007). They are also sensitive to species able to modify the mobility of these carriers, and more generally the transport properties in sensitive materials (Jiménez-Cadena et al., 2007).

In our case, studies, led since 2005 in the Microwave Research Team (GERM group) of the University of Burgundy, highlight an innovative transduction method, working at room temperature, based on the propagation of microwaves through sensitive materials. With this method, experiments on the detection of gases like ethanol (Barsan et al., 2007; Chen et al., 2004) and NH3 (Rossignol et al., 2013; Korotcenkov, 2014; Gurlo, 2006) have been led with sensors involving various propagative structures adapted to microwaves and sensitive materials like metal oxides (SnO_2, TiO_2) and organic materials (cobalt phthalocyanines, CoPc).

This transduction technique estimates the evolution of the sensitive material permittivity (Komarov et al., 2005; Ramo et al., 2007) at microwave frequencies as a function of the adsorbed quantity of target gas molecules on the surface of the sensitive layer at room temperature whereas it only operates in the second order in the case of conductimetric transducers.

2. Microwave transduction principle

The microwave transduction is based on the phenomena of propagation and reflection of an incident electromagnetic wave in a material in the range of microwaves. The characteristics of the reflected wave depend on the physical and chemical properties of the material. When a wave crosses a material, its characteristics are modified (modulus, phase). The recovery of this wave allows the characterization of the material with which the wave interacted (Marynowski et al., 2010). The microwave gas sensing transduction is thus based on the measurement of the sensitive material permittivity evolution as a function of the frequency, consecutively to the adsorption of gas molecules at room temperature. We should note that the permittivity of a material evolves with the frequency range of the electromagnetic wave.