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NAP-XPS Study of Ethanol Adsorption on TiO_2 Surfaces and Its Impact on Microwave-Based Gas Sensors Response †

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Abstract: This work presents new elements of understanding for the microwave-based gas sensors behavior at room temperature. A TiO_2-covered microstrip interdigital capacitor was submitted to various ethanol concentrations and showed a proportional response in the 1–10 GHz microwave range. For each concentration and right after ethanol injection, the sensor response presented a slight overshoot which is often found in gas sensors studies. Near ambient pressure photoemission experiments (NAP-XPS) were conducted to explore the physicochemical causes of this overshoot, and demonstrated the formation of an ethoxide during ethanol adsorption.

Keywords: ethanol adsorption; NAP-XPS; microwave-gas sensors

1. Introduction

Microwave-based gas sensors rely on a transduction principle which can meet two major challenges of sensors research. First, they can operate with any type of materials, from amorphous polymers to crystalline metal oxides, regardless of their conducting or insulating properties [1]. This results in their capacity to operate at room temperature, which represents a real advantage in terms of energy consumption and embeddability [1]. Second, measurements are made over a whole frequency range, which multiplies the information collected during sensing experiments. This opens the perspective of a multivariable sensor which can be useful for a multipurpose sensor configuration [2,3].

In this work, titania nanoparticles (P25 Degussa) were deposited on the sensor surface via a low cost tape casting technique. The sensor propagative structure consists in a microstrip interdigital capacitor designed to operate in the 1–10 GHz microwave range and optimized by finite element simulation with Ansys High Frequency Structural Simulator (HFSS) (inset of Figure 1). The reflection and transmission coefficients of the sensor were tracked in real time during the experiment. The frequency with the highest sensitivity to ethanol has been determined at 2.38 GHz following the data processing described in [4]. This frequency is highlighted in Figure 1.

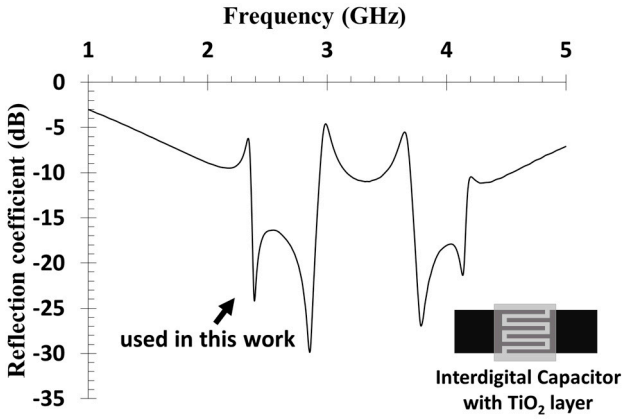

Figure 1. Reflection coefficient (S_{11} dB) of the sensor covered with a layer of TiO_2 nanoparticles. Inset: design of the sensor (interdigital capacitor).

2. Microwave Experiment

Experiments were firstly conducted with 4 min exposure periods of pure argon flow, alternated with 1 min periods at desired ethanol concentrations in argon flow (from 50 to 250 ppm). The reflection coefficient evolution at 2.38 GHz clearly demonstrates that the sensor response is proportional to the ethanol concentration (Figure 2). The response time is under 40 s for each concentration, while the recovery time is under 180 s.

Experiments were then carried out by increasing the ethanol exposure period up to 5 min (inset of Figure 2). In this case, the sensor response exhibits a slight overshoot which is usually attributed to secondary reactions or diffusion–reaction phenomena [5]. However, the amplitude of this overshoot is reduced by multiplying the number of concentration pulses. Therefore, NAP-XPS experiments were conducted to investigate the physico-chemical interface processes that may explain this behavior.

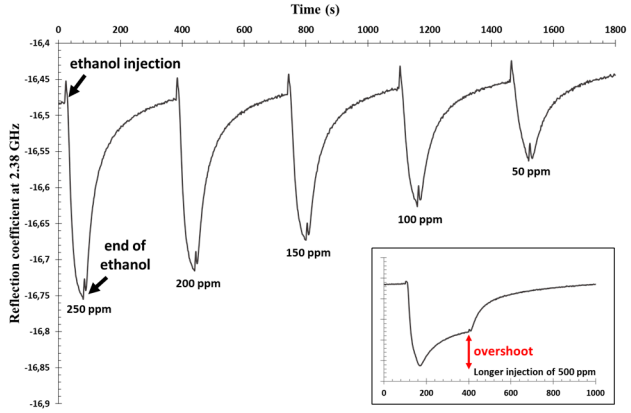

Figure 2. Evolution of the reflection coefficient at 2.38 GHz for 1 min exposures of diluted ammonia (50 to 250 ppm) and 5 min of pure argon. The inset shows the evolution for a 5 min exposure at 500 ppm of ammonia.

3. NAP-XPS Study of Ethanol Adsorption

Near ambient pressure photoemission experiments (NAP-XPS) were conducted to explore the physicochemical causes of this overshoot. The C1s line decomposition highlighted the appearance of a small carbon doublet (286.5 and 285.0 eV). These two peaks are consistent with the formation of an ethoxide on the surface, due to ethanol exposure. (Figure 3). This observation is consistent with previous report, where ethanol was submitted to titania surfaces under FT-IR investigations [6]. Nonetheless, the majority of the ethanol is physically adsorbed on the surface. Thus, a small portion

of the ethanol phase is chemically adsorbed on the TiO_2 surface while the remainder is physically adsorbed. This two-step behavior explains the overshoot in the sensor response.

Indeed, most of the ethanol is physically adsorbed. This explains the relatively good reversibility of the sensor since the physisorption is reversible, even at room temperature. The small part of chemical adsorption is due to the ethoxide formation. Since chemisorption is not reversible, especially at room temperature, the ethoxide accumulates on the surface and does not desorb after the end of ethanol exposure. Thus, the presence of this small chemisorbed phase explains the appearance of the overshoot during the first exposures to ethanol, and its disappearance after a few concentrations pulses.

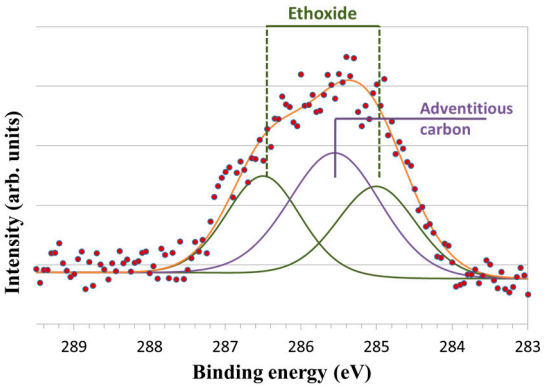

Figure 3. C1s core level line recorded by XPS after ethanol exposure (up to 5 hPa) at room temperature, followed by back to ultra-high vacuum. Adventitious carbon peak corresponds to the carbonaceous layer usually found in the surface or air exposed samples.

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Conflicts of Interest: The authors declare no conflict of interest.

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