Ozone Sensors Based on WO$_3$ Sputtered Layers Enhanced by Ultra Violet Light Illumination

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Abstract—**In this work, the conductance behavior of tungsten trioxide based chemoresistive ozone sensors under ultra violet illumination was investigated. The tungsten trioxide sensitive layers were deposited on a SiO$_2$/Si substrate by reactive radio frequency magnetron sputtering with several Argon / Oxygen ratios. The detection principle is based on a change in the conductance of the semiconductor oxides when ozone is present around the surface. We demonstrate the influence of Argon / Oxygen during the deposition of the sensitive layer, on ozone detection at 50°C under light illumination. The sensor shows good sensitivity to ozone, with a stable baseline, fast response and recovery time. These results are promising for the detection of ozone at low temperature.**

Keywords-Gas sensors; UV activation; Electronic traps; Ozone; Environment; Health.

I. INTRODUCTION

Tungsten trioxide (WO$_3$) sensitive layers have been shown to be an effective material for ozone (O$_3$) detection [1]. Metal oxides present good sensitivity, long term stability and low cost production. However, their high operating temperature (around 280°C) is a drawback, as it increases their power consumption, affects the ageing of the materials and compromises their use on flexible substrates. Nevertheless, some metal oxides, such as zinc oxide (ZnO) or WO$_3$, exhibit photo-catalytic behavior [2]-[3] which can lower their optimal detection temperature by supplying them with energy in the form of Ultra Violet (UV) light radiation. This work is dedicated to experimental detection of ozone at 50°C under UV illumination using a WO$_3$ sensing layer. The paper is structured as follows: in Section II, we will describe the sensors and the experimental set up; then, in Section III, the sensing results will be discussed based on our measurements in dark and under UV light illumination in ozone environments. Finally, a conclusion is drawn in Section IV.

II. DESCRIPTION OF APPROACH AND TECHNIQUES

This section is composed of two parts: one section is dedicated to the sensing film fabrication, while the other is devoted to the measurement system set-up.

A. Gas sensors

The gas sensor is based on a transducer made of Ti/Pt interdigitated electrodes (5 and 100 nm thick, respectively) spaced by 50 μm (Figure 1) deposited on Si/SiO$_2$ substrate. The WO$_3$ sensitive layer, about 50 nm thick, was deposited by reactive Radio Frequency (RF) magnetron sputtering. The Argon (Ar) / Oxygen (O$_2$) ratio was changed as shown in Table I. All samples were deposited at a power of 115 W under a total pressure of 3.10^{-3} mbar.

TABLE I. ARGON / OXYGEN PLASMA RATIO OF SAMPLES PREPARED BY RF SPUTTERING

Samples	EC	EB	ED
Ar/O$_2$ ratio	3 : 2	1 : 1	2 : 3

All these samples, named EC, EB and ED series in our experiments, were then annealed in ambient air at a temperature of 400°C for two hours to improve their nano-crystallization and stability.
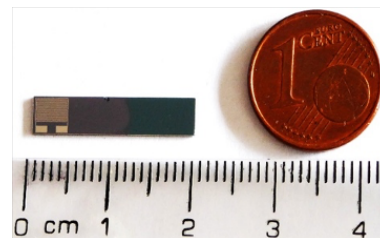

Figure 1. Sample image of SiO$_2$/Si substrate (4 x 4 mm^2) with platinum electrodes and a trioxide tungsten layer above it

The film structures were determined by X-Ray Diffraction (XRD) with a Philip's X'Pert MPD equipment (λ = 1.54 Å). Chemical composition measurement was performed using Energy Dispersive X-ray Spectroscopy (EDS) on a Zeiss GeminiSEM 500 ultra high resolution Field Emission Scanning Electron Microscope (FESEM). An Energy dispersive analysis of X-rays (EDAX) Octane Silicon Drift Detector (129 eV energy resolution for Manganese) was used at 5 kV with a magnificence of 350 and 10k.

B. Experimental Setup for Sensor Characterization

Our test bench consists of a gas generation unit, a test chamber with a Light Emitting Diode (LED UV5TZ-390-30) and a Keithley Model 2450 Source Measure Unit (SMU) (Keithley, U.S.A.) monitored by a homemade LabVIEW program. The gas sensing properties were investigated by

measuring the microsensor resistance in a closed thermo-regulated test chamber. The experimental set-up allows the sensors to be tested in dry air and diluted gas. Ozone is produced with an O_3 generator model 165 from Thermo Environmental Instruments and its concentration is measured using an O_3 analyzer model 49 from Thermo Environmental Instruments. In all experiments, the gas flow rate was maintained at 500 sccm (Standard Cubic Centimeters per Minute). For each concentration, the sensors were exposed to the gas for 60 s and their temperature was kept constant at 50°C. The distance between the UV LED and the microsensor was kept constant to allow a 1.5 mW/cm^2 measured power density at the sensor surface. Figure 2 shows a sensor under irradiation from a UV LED.
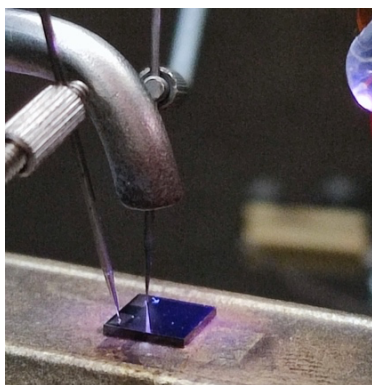

Figure 2. A sensor under UV illumination.

III. RESULTS AND DISCUSSIONS

The experiments were conducted in a laboratory environment. In this section, we will discuss our morphological and electrical results.

A. Chemical Composition

The XRD diffractograms of WO_3 films (Figure 3) show the presence of crystalline layers with monoclinic phase WO_3 [4].
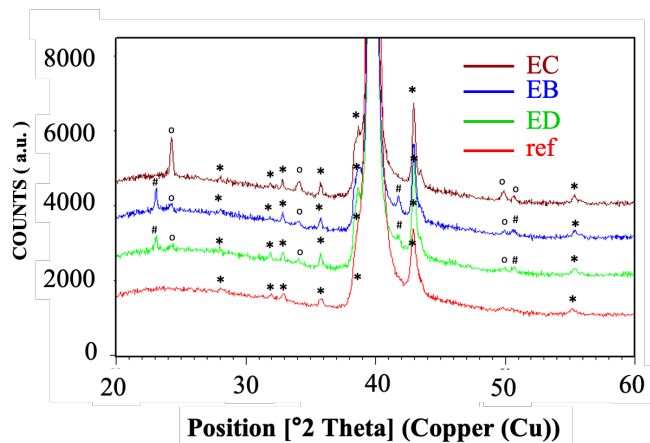

Figure 3. Comparison of WO_3 diffractograms with reference test platform (*) using λ = 1.54Å (Philip's X'Pert MRD).

A diffractogram was performed on the test platform with the interdigitated electrodes (Ti/Pt) deposited on SiO_2/Si substrate without the trioxide layer, to be used as a reference diffractogram. The diffractogram comparison of the samples with the metal oxide layers demonstrates the presence of two grain orientation families, identified on the figure 3 with the symbols # and o. All the diffraction peaks are compatible with the monoclinic structure of WO_3. But it seems that depending on the Ar/O_2 ratio used during the sputtering, the growth of grains with different orientations are favored. Particularly, the lowest oxygen ratio sample (EC) does not present the peaks identified on the figure as #. Three EDX measurements were carried out on the same sample at two different magnifications: x350 on WO_3 on three different electrodes and x10,000 on WO_3 on one electrode. The analyzed areas were 3 μm by 3 μm. To avoid the SiO_2 interferences on our WO_3 chemical measurements, preliminary tests were performed on platinum electrodes. A 5 kV electron beam energy was used for all the analysis. Energy Dispersive X-Ray (EDX) Spectroscopy measurements show that for this electron beam energy and 100 nm thick platinum electrode, no silicon element was detected. Thus, by performing our measurements on WO_3 with a platinum electrode underneath, no incertitude was induced by the SiO_2 substrate. When analyzing these results, no clear variation was observed on the chemical composition of the films for both magnifications. The WO_3 material maintains a near-stoichiometric composition over the whole deposition range with a ratio of nearly 77%O and 23%W (standard deviation of 0.5%). Auger electron spectroscopy (AES) analyses carried out in another study [5] demonstrated that the O/W ratio can indeed be altered by varying the oxygen content of the plasma, but that after annealing in air, the disparities tend to disappear. Thus, whatever the oxygen value used in our plasma, a quasi-stoichiometric ratio was observed. These results are in agreement with literature [5]-[8] where X-Ray Photoelectron Spectroscopy (XPS) analyses of WO_3 layers deposited under several conditions show that the chemical composition of WO_3 remains stoichiometric unless other chemical species are used during the annealing.

B. Gas Detection under UV illumination

Semiconducting metal oxides are the most commonly used sensing materials for gas detection. They are cheap, stable, highly sensitive and need low maintenance. Nevertheless, energy activation is required to facilitate the chemical reaction on their surface and induce a change in carrier concentration upon exposure to gas molecules. Thus, their electrical conductance changes. In this work, we used a light activation to study the WO_3 photocatalytic properties at 50°C. The effect of visible and UV lights on the detection properties of WO_3 can be described as the result of two mechanisms. The first one occurs at low photon energies. Oxygen ions (O_2^-) are chemically bound to the surface with the free charge carriers of the material, electrons. This binding

is of the order of 1.50 eV. Therefore, when the WO_3 surface is irradiated by a photon source with an energy higher than 1.50 eV, oxygen species capture the photons and desorption occurs, releasing charge carriers and increasing the conductance of the material. This increase is generally small (drop is less than a factor of 10 in the resistance) and does not allow for rapid and repeatable detection. The second mechanism is added when the photon energies are higher than the indirect band gap of WO_3, of the order of 2.6-2.8 eV: the creation of electron-hole pairs. These pairs increase the density of free charge carriers and participate in the desorption of oxygen atoms [9]-[11]. A large increase in conductivity is achieved (about a factor of $10^2 - 10^3$) and a large proportion of surface sites are unoccupied. Upon injection of ozone into the test chamber, the reactive gas molecules begin to occupy the free surface sites and bind to the free charge carriers, creating a depletion zone that increases the resistivity. Figure 4 shows a UV LED spectrum produced by our Avantes spectrometry equipment at room temperature (25°C).
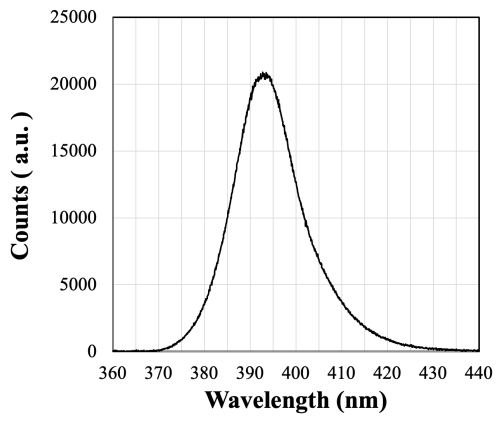

Figure 4. UV LED Spectrum

We observe a broad peak centered at 393 nm corresponding to the UV LED used in our experiments. The maximum intensity is reached around 393 nm which corresponds to a maximum energy of 3.16 eV calculated with formula (1):

$$E = h * c / \lambda \tag{1}$$

where h is the Planck constant, c the light speed and λ the wavelength.

Thus, according to the literature, there is both desorption of oxygen and creation of electron-hole pair. This hypothesis was confirmed by the decrease in resistance when our sensor was exposed to UV light.

The normalized response of the sensor is defined in (2) as the ratio of the sensor resistance under the O_3 exposure to the sensor resistance in dry air:

$$R = R_{gas} / R_{air} \tag{2}$$

where R_{air} is the sensor resistance through dry airflow and R_{gas} the sensor resistance in the presence of O_3.

Figure 5 shows the detection properties towards O_3 of the EB sample made with an Ar/O_2 gas ratio 1:1, as generally reported in the literature [7], [12] under UV light and darkness.
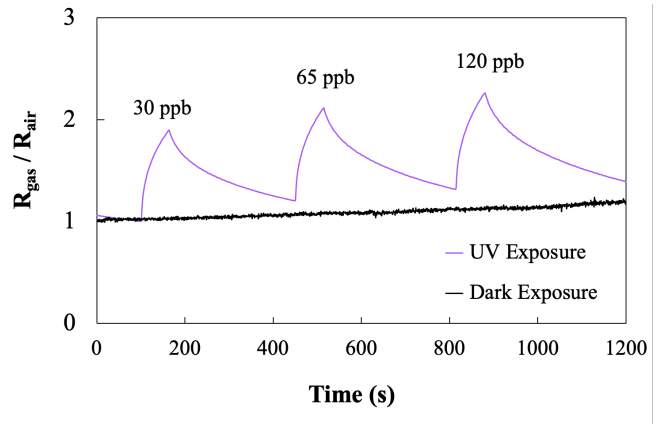

Figure 5. Ozone detection, at an operating temperature of 50°C, in dark and under UV illumination for a WO_3 film prepared with a 1:1 Ar/O_2 ratio.

In darkness and at low temperature maintained at 50°C, the optimal conditions for chemisorption reaction are not reached, so no adsorption or desorption of oxygen species (O^{2-} or O_3) can occur. The "Dark Exposure" curve shows a constant baseline and no response is observed for all ozone exposures of 30 ppb, 65 ppb and 120 ppb, respectively. Under UV illumination and at 50°C, desorption of O^{2-} by absorption of UV photon occurs and electron-hole pairs are created, thus chemical reaction becomes possible. The "UV Exposure" plot indicates a normalized response of 1.89, 2.10 and 2.25 reached for 60 s ozone exposure at 30 ppb, 65 ppb and 120 ppb, respectively. Stabilization was incomplete for response and recovery as chemisorption remains a slow process and ten minutes were generally required [9], [13].

Figure 6 illustrates the sensors responses to 30 ppb ozone for several Ar/O_2 gas ratios in the sputtering deposition process.
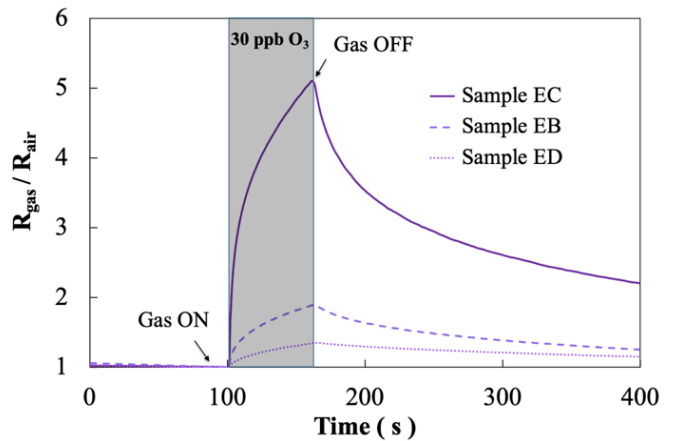

Figure 6. Comparison of Ozone (30 ppb) detection by our samples. Measurements under UV illumination for an operating temperature equals to 50°C.

The EB sample made with an Ar /O_2 gas ratio of 1:1 shows a response of 1.89 for an ozone concentration of 30 ppb. By increasing the oxygen content during the plasma process, the sensor response to ozone is found to decrease, and a normalized response of 1.35 is achieved for 30 ppb of O_3. On the contrary, by decreasing the oxygen content, the sensor response to ozone increases, and a normalized response of 5.10 is achieved for 30 ppb of O_3.This trend is maintained for other ozone concentrations as show in figure 7.
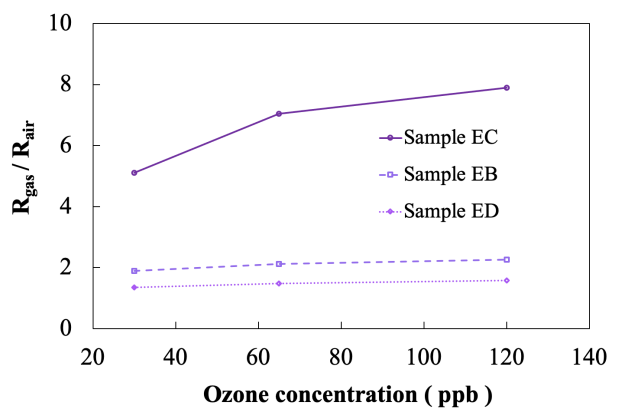

Figure 7. Response of three sensors to ozone concentration variation, under UV illumination at an operating temperature of 50°C.

The lowest oxygen ratio sample has the highest normalized response to ozone of 5.10, 7.04 and 7.90, which is promising for ozone detection at low temperature, while the highest argon ratio sample has the lowest normalized response of 1.35, 1.47 and 1.59 for 30 ppb, 65 ppb and 120 ppb, respectively.

IV. CONCLUSION AND FUTURE WORK

This work reports our preliminary results on ozone sensors, based on a WO_3 sputtering layer, operating at 50°C under UV light detection. Our results demonstrated that the Ar/O_2 ratio used during the layer deposition did not affecting the chemical stoichiometry after annealing at 400°C during 2 h. However, XRD measurements showed that several preferential grain orientations were formed during the layer fabrication depending on the Ar/O_2 ratio during the WO_3 sensitive layer deposition. Our results demonstrate that the choice of the best Ar/O_2 ratio during the WO_3 sensitive layer fabrication will allow to optimize the ozone detection at low temperature by light illumination. Complementary XPS measurements will be performed to understand the influence of oxygen vacancy on our results.

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