

# On-line monitoring of CO<sub>2</sub> quality using doped WO<sub>3</sub> thin film sensors

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## Abstract

Thin films of either pure or doped tungsten oxide were grown by radiofrequency (rf) sputtering onto silicon micromachined substrates. Up to 7 different dopant materials (noble metals or metal oxides) were deposited by rf sputtering or by evaporation onto the tungsten oxide films. The responsiveness of the resulting micromachined sensors towards sulfur dioxide and hydrogen sulfide was studied. Other pollutants in CO<sub>2</sub> such as ethylene and methane were also tested. It was found that Au-doped tungsten oxide sensors were highly sensitive to H<sub>2</sub>S, poorly sensitive to SO<sub>2</sub> and almost insensitive to hydrocarbons. On the other hand, Pt-doped tungsten oxide was highly sensitive to SO<sub>2</sub>, poorly responsive to H<sub>2</sub>S and nearly insensitive to hydrocarbons. By applying a principal component analysis (PCA), we show that it would be possible to selectively detect traces of H<sub>2</sub>S and SO<sub>2</sub> in a CO<sub>2</sub> stream using doped WO<sub>3</sub> microsensors. These sensors could be used in a low-cost analyzer of beverage-grade CO<sub>2</sub>.

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## 1. Introduction

In recent years, there has been a continuous improvement towards quality assurance in the beverage industry. The International Society of Beverage Technologists (ISBT) has established quality guidelines for carbon dioxide used in beers, mineral waters and soft drinks [1]. Carbon dioxide can be produced from a wide variety of processes. Each process has the potential of leaving residues that reduce the purity of CO<sub>2</sub>. Furthermore, contaminants may be introduced from storage or transport vessels. In the quality control of CO<sub>2</sub>, the methods generally used are analytical techniques such as gas chromatography or gas chromatography coupled to mass spectrometry (GC/MS) [2]. However, these techniques are very expensive and bulky. That is why, a low cost, small size analyzer to monitor on-line the quality of CO<sub>2</sub> would be of great interest, especially for breweries or soft drink companies, where acquiring a GC/MS system is out of question. On this basis,

equipment based on an array of metal oxide gas sensors would be a good solution that could be installed in any beverage production plant.

It is well known that atmospheric oxygen plays an important role in gas detection by metal oxide gas sensors [3,4]. Kohl [5] reported some surface processes for the detection of reducing gases, which did not require the presence of atmospheric oxygen. In the last years, several groups have investigated the sensing mechanism of metal oxides operated under low oxygen concentrations [6] and in streams of inert gases such as argon [7]. In 2003, Vilanova et al. [8,9] developed a multisensor system (tin oxide sensors doped with noble metals) to detect methane, ethylene and sulfur dioxide in a CO<sub>2</sub> stream. However, these sensors (based on SnO<sub>2</sub>) showed low sensitivity to sulfur compounds, especially to H<sub>2</sub>S. That is why, a system based on WO<sub>3</sub> sensors (pure and doped with platinum) was developed for the detection of sulfur species in carbon dioxide [10]. In this paper, we further study the detection of sulfur compounds in CO<sub>2</sub> by analyzing the effect of 7 different dopants on tungsten oxide based sensors. The objective is the selective detection of these compounds at a low operating temperature (below 300 °C).

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## 2. Experimental details

### 2.1. Sensor fabrication

Four element microhotplate sensor arrays were fabricated. Details on the design and fabrication can be found in a previous article [10]. The active layer of  $\text{WO}_3$  was radiofrequency (rf) sputtered and patterned by lift-off. The deposition was made using a target of W (99.95% of purity) that was fixed at 70 mm from the substrate. The substrate was kept at room temperature during the process. The sputtering atmosphere consisted of 1:1  $\text{Ar}/\text{O}_2$ . The forward input power was maintained at 200 W with zero reflected power. The pressure in the chamber during deposition was 0.5 Pa. After the deposition of tungsten trioxide, the active layer was doped. As doping materials, the following compounds were used: Pt, Au, Ag, Ti,  $\text{SnO}_2$ , ZnO and ITO (indium tin oxide). Most of them (Pt, Au,  $\text{SnO}_2$ , ZnO and ITO) were deposited by rf magnetron sputtering. The conditions for these processes are summarized in Table 1. For the deposition of Ag and Ti, an e-gun evaporation was employed. In this last case, the target was placed 17 cm away from the sample. The thickness of each dopant was below 10 nm (layer thickness was estimated by a 4-probe resistance measurement system). As a final step, the active layer was annealed in dry air for 2 h at 400 °C.

### 2.2. Structural analysis

The morphology of platinum-doped  $\text{WO}_3$  active layers was studied by transmission electron microscopy (TEM). The aim of this analysis was to study the surface distribution of dopants and to estimate the thickness of the layer. For this purpose, a film of Pt-doped  $\text{WO}_3$  was deposited directly on a Si wafer. A Si wafer was used instead of a micromachined sensor substrate because the latter would have broken during the measurement process. The film was annealed at 400 °C in air for 2 h. Two samples were prepared for TEM analysis: one of them was cross-sectional and the other was planar. Using the first one, we could estimate the thickness of the layer, while in the second, the surface distribution of the doping material could be observed. Micrographs were taken using a Hitachi H-800-MT microscope equipped with a Gatan Multiscan camera, working at 200 kV. The same equipment was applied to make Selected Area Electron Diffraction (SAED).

The  $\text{WO}_3$  phase was determined also by using X-ray diffraction (XRD). XRD measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing

Table 1  
Deposition conditions used to sputter some of the dopant materials

Dopant	Target	$\text{Ar}/\text{O}_2$ (sccm)	Power (W)	Time
Pt	Pt (99.99%)	14.6/0	50	10 s
Au	Au (99.99%)	14.6/0	100	30 s
$\text{SnO}_2$	Sn (99.95%)	7/7	100	2 min 30 s
ZnO	Zn (99.99%)	7/7	100	10 min
ITO	ITO (99.99%)	14/0	50	4 min

The sputtering pressure was 5 Pa for all the processes. sccm – standard cubic centimetre per minute.

Table 2

Typical contaminants with their maximum concentrations allowed in 99.95% purity  $\text{CO}_2$  (after ISTB [1])

Pollutant	Maximum allowed concentration
Sulfur dioxide	2 ppm
Hydrogen sulfide	500 ppb
Other sulfur compounds	500 ppb
Nitrogen dioxide	2.5 ppm
Nitric oxide	2.5 ppm
Ammonia	2 ppm
Nitrogen	40 ppm
Carbon monoxide	2 ppm
Benzene	20 ppb
Methane	30 ppm
Heavy hydrocarbons	1 ppm
Volatile hydrocarbons	20 ppm
Total aldehydes	200 ppb
Oxygen	9 ppm
Water	8 ppm

geometry and vertical  $\theta$ – $\theta$  goniometer) fitted with a grazing incidence ( $\omega=0.52^\circ$ ) attachment for thin film analysis and scintillation counter as a detector. The angular  $2\theta$  diffraction range was between  $21.0^\circ$  and  $70.0^\circ$ . The data were collected with an angular step of  $0.05^\circ$  at 3 s per step and sample rotation.  $\text{Cu}_{K\alpha}$  radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

### 2.3. Gas sensitivity measurements

The sensors were introduced in a temperature controlled, 16-ml chamber. First, pure  $\text{CO}_2$  (90 ml/min) flowed through the chamber and the sensor baseline was established. Then the stream was switched (by the means of electrovalves) to  $\text{CO}_2$  with a given contaminant (from calibrated bottles). During all the measurements, the sensor resistance was acquired and stored for further processing. Four contaminants were tested, namely, 1 ppm  $\text{SO}_2$ , 100 ppb  $\text{H}_2\text{S}$ , 30 ppm  $\text{CH}_4$  and 20 ppm  $\text{C}_2\text{H}_4$ . These concentrations were chosen based on the maximum allowed in beverage-grade  $\text{CO}_2$  according to ISBT (see Table 2). The sensors were operated at 110, 200 and 260 °C. Each pollutant was measured at the different operating temperatures. Every measurement was replicated ten times.

## 3. Results and discussion

### 3.1. Active layer characterization

First, the cross-sectional sample was studied (Fig. 1(a)). From this image, the thickness of the Pt film was estimated to be 3–4 nm. This thickness was less than the expected value (about 10 nm). The expected value was extrapolated based on previous depositions on Si wafers and four-point measurements of layer resistance. It is well known that growth rate is not a linear function of time. Our deposition process took 10 s and, in such a short interval, it is very difficult to control the growth process. We assume that this is the reason to obtain a layer thinner than expected. However, we were interested in obtaining a very thin

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