Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 105 (2005) 271–277
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

# Influence of the annealing and operating temperatures on the gas-sensing properties of rf sputtered $WO_3$ thin-film sensors

M. Stankova [a], X. Vilanova [a], E. Llobet [a,*], J. Calderer [b], C. Bittencourt [c], J.J. Pireaux [c], X. Correig [a]

[a] *Departament d'Enginyeria Electrònica, Elèctrica i Automàtica, Universitat Rovira i Virgili, Avda. Països Catalans 26, 43007 Tarragona, Spain*
[b] *Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya, c/Jordi Girona 1-3, 08034 Barcelona, Spain*
[c] *Laboratoire Interdisciplinaire de Spectroscopie Electronique, Falcultés Universitaires Notre Dame de la Paix, 61 Rue de Bruxelles, B-5000 Namur, Belgium*

Received 10 February 2004; received in revised form 7 May 2004; accepted 4 June 2004
Available online 22 July 2004

**Abstract**

The sensing properties of $WO_3$ thin films deposited by rf sputtering onto silicon substrates have been investigated. After deposition, the films underwent an annealing process in dry air that lasted 24 h. Three different annealing temperatures (350, 400 and 450 °C) were used to analyze the influence of this parameter on the sensor response. The morphology and composition of the films were studied by AFM and XPS. The films were found to be essentially inhomogeneous. The oxygen-to-tungsten atomic ratio of the active layers reveals that, irrespective to the annealing temperature used, the $WO_3$ active layers were close to their stoichiometric formulation, although a tendency to loose oxygen atoms at the higher annealing temperatures tested was inferred. The sensitivity of the films to ammonia, nitrogen dioxide, ethanol, benzene, methane and carbon monoxide was studied at three different operating temperatures (300, 350 and 370 °C). By selecting the appropriate annealing and operating temperatures, it was found possible to selectively detect nitrogen dioxide in the presence of ethanol and ammonia, or to detect ammonia in the presence of ethanol.


*Keywords:* Metal oxide gas sensors; Tungsten oxide; Ammonia; Nitrogen dioxide

## 1. Introduction

In the last years, there has been a growing interest for the control of air pollutants and monitoring of toxic gases. Ammonia emissions such as those produced by agricultural activities (e.g. livestock buildings [1]) are a major environmental problem, particularly in the neighborhood of urban settlements. Related also to environmental concern, a potential need of ammonia sensors is found for combustion exhaust control in power plants, where $NO_x$ is removed by a chemical treatment with $NH_3$ over catalysts [2]. Also the need of gas sensors suitable for safety and industrial process control applications has been raised. In particular, there is an increasing need to detect low concentrations of air pollutants like $NO_x$. Nitrogen oxides are pollutants that are encountered frequently in everyday life, and are produced by combustion facilities and vehicles. Nitrogen oxides are known to be extremely harmful to the human body. The permissible exposure levels, which are the time-weighted average concentrations that must not be exceeded during an 8-h work shift of a 40-h workweek (established by the OSHA [3]), are set to 25 and 5 ppm for ammonia and nitrogen dioxide, respectively.

Semiconductor gas sensors are a particularly interesting option for the detection of ammonia and nitrogen oxides, because they are sensitive enough to detect trace pollutants in air at the ppm level, and because of their structural simplicity, low cost and small size. Among semiconductor metal oxides, tungsten trioxide (a wide bandgap n-type semiconductor) has been shown to be sensitive both to $NH_3$ and $NO_x$ [4–15]. Tungsten is a transition metal that can be found at different oxidation states ($W^{4+}$, $W^{5+}$, $W^{6+}$) enhancing the oxidizing properties of $NO_2$ at the surface of tungsten oxide.

$WO_3$ films can be deposited by means of different techniques such as reactive rf sputtering, thermal evaporation, chemical vapor deposition, screen-printing, drop coating and sol–gel methods. The working mechanism of $WO_3$-based

* Corresponding author. Tel.: +34-977-558502; fax: +34-977-559605.
*E-mail address:* ellobet@etse.urv.es (E. Llobet).

0925-4005/$ – see front matter. 
doi:10.1016/j.snb.2004.06.009

sensors lies in changes of the oxide film resistance resulting from physisorption, chemisorption and catalytic reactions of gas-phase species at the surface of the film. The sensitivity of $WO_3$ to $NH_3$ and $NO_2$ heavily depends upon film parameters such as composition, morphology (e.g. grain size) and microstructure (e.g. porosity, surface-to-volume ratio). Film parameters are related to the deposition technique used, the deposition conditions and the subsequent annealing process. Annealing, which is an essential process to obtain stable films with well-defined microstructure, causes stoichiometry and microstructural changes that have a high influence on the sensing characteristics of the films [16].

In a previous work [17], we studied the effects of the oxygen partial pressure and the annealing temperature on the composition, morphology and ammonia sensitivity of rf sputtered tungsten trioxide films. On the basis of this study, it was found that the samples deposited with an Ar:$O_2$ partial pressure ratio of 1:1 and annealed at 350 °C showed the highest sensitivity to ammonia vapors.

In this work, $WO_3$ films have been grown by rf sputtering with an Ar:$O_2$ partial pressure ratio of 1:1 and annealed at different temperatures. Their morphology and composition have been studied by atomic force microscopy (AFM) and X-ray photolelectron spectroscopy (XPS) and their gas-sensing properties to ammonia, nitrogen dioxide, ethanol, benzene, methane and carbon monoxide have been investigated. The objective of the study was to find a route towards sensitive but also selective tungsten trioxide-based sensors for ammonia and nitrogen dioxide detection.

## 2. Experimental

### 2.1. Sensor fabrication procedure

#### 2.1.1. Sensor substrate

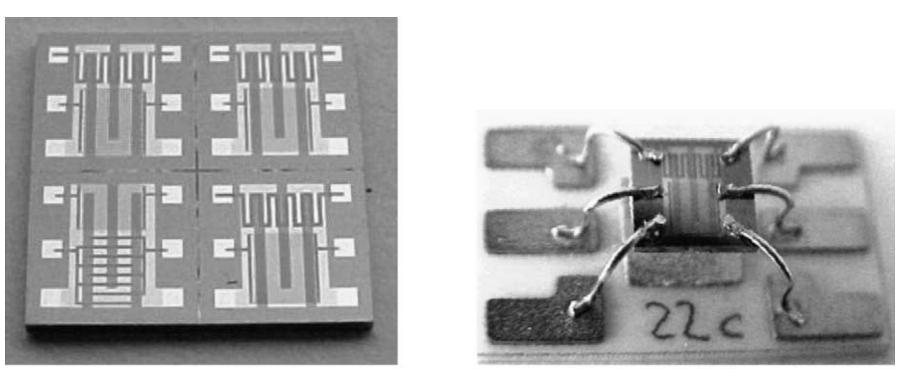
The sensors were fabricated on silicon wafers using microelectronic technology. We choose a silicon substrate with buried resistor to be used as a heater, two interdigited electrodes and a resistive temperature sensor. Our choice was due to the simplicity of the structure and the fabrication processes. We used an n-type silicon wafer ⟨1 0 0⟩. First, a layer of $SiO_2$ was grown by thermal oxidation. Then a layer of NiCr (80:20%) was deposited and patterned to make a substrate-heating resistor. In the next stage an insulating layer of PSG/$SiO_2$ was deposited by PECVD. Next, a Ti/Au film was evaporated and patterned to form a pair of interdigited electrodes and a resistor to be used as a temperature sensor (see Fig. 1a). A summary of the characteristics of the substrates fabricated is shown in Table 1. The resistance of the temperature sensor, $R_T$, was used to monitor the power to be supplied to the substrate heater to keep the sensor at the desired operating temperature. By measuring the resistance value of a Ti/Au meander, which has a known temperature coefficient of resistivity, the temperature of the sensor could be derived.

Table 1
Characteristics of the sensor substrate

| | |
|---|---|
| Substrate dimension | 5 mm × 5 mm |
| Dimension of the active layer | 2.5 mm × 3 mm |
| Heater resistance (at room temperature) | 230 ± 2.0 Ω (average value for 48 sensors) |
| Temperature sensor resistance, $R_0$ | 120 ± 5.2 Ω |
| Temperature coefficient of resistivity, $\alpha$ | $1.11 \times 10^{-3}$ °C$^{-1}$ |

#### 2.1.2. Active layer

The gas sensitive $WO_3$ layer was deposited on top of the previous substrate structure using reactive rf magnetron sputtering at room temperature. We used a pure tungsten target (99.95%) and plasma of argon and oxygen gas (Ar:$O_2$ = 50:50%, which were found to be the best deposition conditions [17]). To define the active layer on the top of the sensor structure a lift-off method was used. The sensors were annealed in dry air for 24 h at three different temperatures 350, 400 and 450 °C, in order to analyze the influence of the annealing temperature on the sensor response to the gases studied. Finally, the sensors were mounted on alumina supports for their subsequent characterization. Fig. 1b shows a sensor substrate prepared for running test measurements.




(a) (b)

Fig. 1. Picture of the sensor substrate: (a) four substrates (before dicing); (b) a mounted sensor.