Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 106 (2005) 713–718
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Impedance spectroscopy on WO_3 gas sensor

A. Labidi[a,b], C. Jacolin[a], M. Bendahan[a], A. Abdelghani[b], J. Guérin[a], K. Aguir[a,*], M. Maaref[b]

[a] *Laboratoire Matériaux and Microélectronique de Provence L2MP (CNRS UMR 6137), Service 152, FST de St Jérôme, Université d'Aix-Marseille III, 13397 Marseille Cedex 20, France*
[b] *Unité de Recherche de Physique des Semiconducteurs et Capteurs, IPEST, BP 51 La Marsa 2070, Tunis, Tunisia*

Received 24 May 2004; received in revised form 1 September 2004; accepted 21 September 2004
Available online 2 November 2004

Abstract

Tungsten trioxide (WO_3) is considered as one of the most interesting materials in the field of gas sensors based on metals oxides semiconductors. We have shown in previous papers [K. Aguir, C. Lemire, D.B.B. Lollman, Electrical properties of reactively sputtered WO_3 thin films as ozone gas sensor, Sens. Actuators B 84 (2002) 1–5; C. Lemire, D.B.B. Lollman, A.A. Mohammad, E. Gillet, K. Aguir, Sens. Actuators B 84 (2002) 43–48 [2]; M. Bendahan, R. Boulmani, J.-L. Seguin, K. Aguir, Characterization of ozone sensors based on WO_3 reactively sputtered films: influence of O_2 concentration in the sputtering gas and working temperature, Sens. Actuators B 100 (2004) 320–324] that structural and surface morphology of tungsten trioxide (WO_3) thin films, prepared by RF sputtered, plays an important role in the gas detection mechanism. In this paper we have studied the impedance evolution of WO_3 sensors versus time and working temperature, under dry air or/and ozone. The AC impedance spectroscopy is a powerful method to understand the nature of conduction processes and the mechanism of gas/solid interactions. The Nyquist response of the sample, as well as under dry air as well as under 0.1 ppm of O_3, have been decomposed on *R–C* parallel circuits. Then, we have shown, that the adsorption of oxygen mainly affects the characteristics of the space charge region at the grain boundaries.

Keywords: AC impedance spectroscopy; Gas sensor; Ozone; WO_3

1. Introduction

Measurement and control systems for pollutant and toxic gas emissions gain increasing importance for a sustainable and ecologically responsible development. The growing trend to portable devices induces an increasing demand for miniaturization. Solid-state gas microsensors are a part of this development.

Tungsten trioxide (WO_3) is considered as one of the most interesting materials in the field of gas sensors based on metals oxides semiconductors [4,5]. Most of the recent publications studied the properties of WO_3 under different gases [6,7,1] such as NO_x, CO, H_2S, O_3. For example, good results for NO_2 and H_2S detections, by sensors based on this material have been reported. Most of them concern WO_3 thin films obtained by sputtering [8,9] or thermal evaporation techniques [10,11].

It is known that the resistance of semiconducting thin films used as sensors are strongly influenced by the presence of oxidizing or reducing gases [12]. The surface conductivity of the sensor is modified by adsorption of gas species and related space charge effects. In oxidizing atmosphere, the oxide surface is covered by negatively charged oxygen adsorbates and the adjacent space charge region is electron-depleted: the oxide layer presents therefore a high resistance. Under reducing conditions, the oxygen adsorbates are removed by reaction with the reducing gas species and the electrons are re-injected into the space charge layers: as a result, the oxide layer resistance decreases. Consequently, a good understanding of bulk and grain boundary transport properties is required to optimise development of this material.

* Corresponding author. Tel.: +33 4 91 28 89 73; fax: +33 4 91 28 89 70.
E-mail address: khalifa.aguir@12mp.fr (K. Aguir).

0925-4005/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2004.09.022

The direct current (dc) measurements give information on the global sensor response. However, the alternating current (AC) method offers a powerful tool to examinate the nature of conduction processes and the mechanism of gas/solid interactions, as the processes of different time constants can be distinguished by varying the frequency [13].

Under appropriate conditions, the bulk, grain boundary, and electrode contributions to overall sensor's resistivity can be resolved by exploiting differences in their responses to an applied AC signal of variable frequency [14]. Quantitative informations about each of these contributing regions may be extracted under favourable circumstances by fitting the experimental response to that of an equivalent circuit, which is usually considered to comprise a series of parallel *R–C* elements.

In this investigation, an AC impedance study is used in order to understand the effect of the operation.

2. Experimental procedure

WO_3 thin films were prepared by reactive radio frequency (13.56 MHz) magnetron sputtering, using a 99.9% pure tungsten target. The films were sputtered on SiO_2/Si substrates with platinum electrodes, in a reactive atmosphere of oxygen–argon mixture gas. The film thickness was around 50 nm. As WO_3 layers are highly resistive, interdigitated electrodes were used in order to reduce the sensor resistance. They were obtained from a sputtered Pt film, using photolithography and lift off processes. After WO_3 deposition on the Pt electrodes, the films were annealed at 450 °C for 1 h in air in order to stabilize the chemical composition and the crystalline structure. Bragg–Brentano ($\theta - 2\theta$) X-ray diffraction (XRD) was applied to check the crystallinity and the structure of the films. Cu Kα radiation ($\lambda = 0.154$ Å) and 0.02° angle step were used for the XRD analysis.

To investigate the ozone sensing properties of WO_3 films, the sensors were introduced in a test chamber allowing the control of the sensor temperature under variable gas concentrations. Dry air was used as a reference gas at a constant total flow of 30 l/h. Ozone gas was generated by oxidising oxygen molecules of a dry air flow exposed to a pen-ray UV lamp. The operating temperature of the sensors was adjusted between 150 and 375 °C.

Complex impedance and resistance measurement data of the sensors at different temperatures, were acquired using a Solartron 1250 frequency response analyser coupled to an impedance adapter, used in order to adapt the high output sensor's impedance to the Solartron's low impedance, in the 50 mHz–65 kHz frequency range. We will note Z', the real part and Z'', the imaginary part of the complex impedance.

3. Results and discussion

3.1. Chemical composition, structure and morphology

X-ray diffraction patterns for the same WO_3 film, before and after annealing at 450 °C during 1 h, show that as-deposited WO_3 films were amorphous whereas annealed films were polycrystalline. Suppose that the crystallographic structure were monoclinic, the parameters deduced from the XRD spectra were: $a = 7.307$ Å; $b = 7.523$ Å; $c = 7.685$ Å and $\beta = 90.60°$. They are in good agreement with the one found in the literature (JCPDS 43-1035).

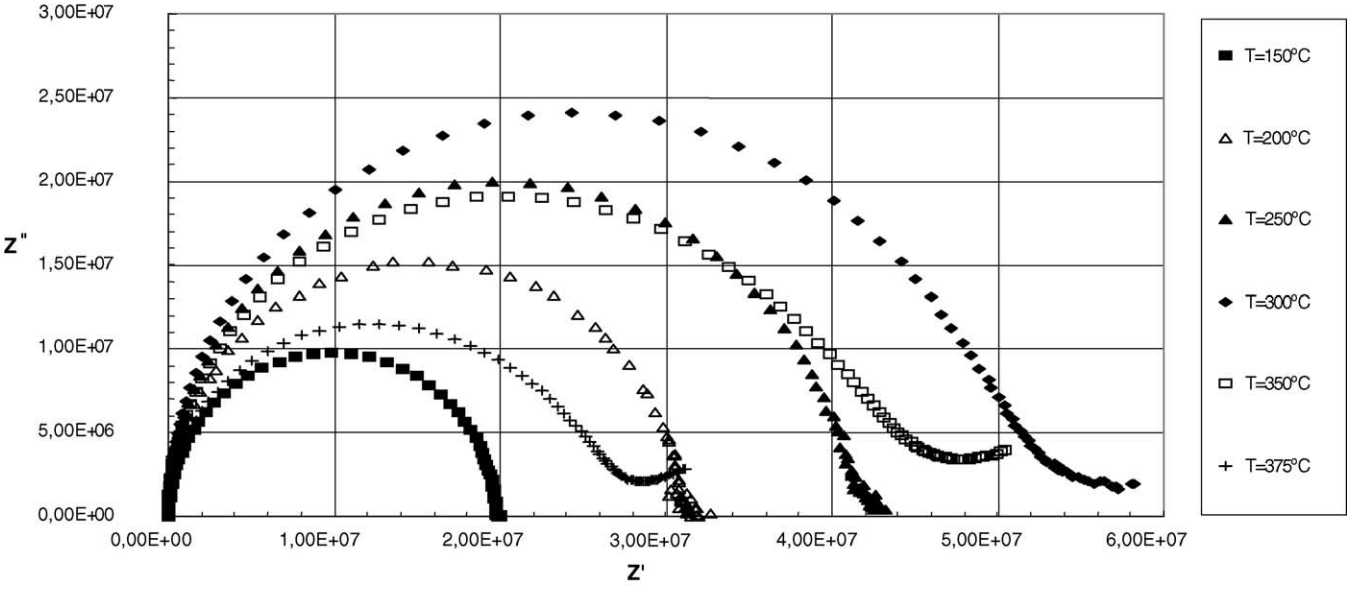

Fig. 1. Impedance variation with the temperature under O_3 (concentration about 0.1 ppm).