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Nanostructured WO_3 deposited by modified thermal evaporation for gas-sensing applications

A. Ponzoni*, E. Comini, M. Ferroni, G. Sberveglieri

SENSOR Laboratory, INFM-Dipartimento di Chimica e Fisica per l'Ingegneria e per i Materiali, Universita' di Brescia, via Valotti 9, 25133 Brescia, Italy

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Abstract

In this work, we present a simple method, based on a modified thermal evaporation technique, to obtain films of nanostructured WO_3 with high surface roughness. This method consists on sublimation from a metallic tungsten wire followed by oxidation in low vacuum conditions and reactive atmosphere (p_{O2}=0.22 mbar), with substrates heated at high temperature (600 °C). Electron microscopy (SEM, TEM) and atomic force microscopy (AFM) analysis revealed that the deposited films are composed of agglomerates with nanometric size and present high surface roughness and large effective area suitable for gas-sensing applications. Sensing measurements highlighted promising performances, particularly at the working temperature of 100 °C: high responses towards sub-ppm concentrations of NO_2 have been observed compared to the lower ones observed for NH_3 and CO. NO_2 tests performed with sensors based on sputtered thin films highlighted that sensors obtained by this thermal evaporation like method exhibit improved performances.

Keywords: Tungsten oxide; Thermal evaporation; Gas sensors

1. Introduction

Tungsten oxide is a widely studied material for the development of solid-state devices based on thin and thick films. The most successful results have been obtained in electrochromics [1,2] and gas sensor fields. Focusing on gas sensors, most of the work has been devoted to conductometric devices, that, due to their small size, low cost production, low power consumption and high compatibility with electronics signal processing are the most promising ones.

The sensing mechanism consists on chemisorption of gaseous molecules on the surface. As a consequence, electrons flow from the surface states to adsorbed molecules and vice versa depending on the gas. Oxidizing gases like NO_2 extract electrons from the conduction band while reducing ones like CO or NH_3 inject electrons.

The sensing properties of a material depend on its microstructure and on the reactivity of its surface. The latter is enhanced by the presence of defects and active species like O^-, O^{2-}, OH^-, H^+ [3]. About the microstructure, it is well established that polycrystalline films exhibit higher performances than amorphous ones [4]. Furthermore, a grain size comparable with the depletion region depth caused by chemisorption strongly enhances the sensitivity [5].

Several materials like SnO_2, TiO_2, ZnO and others have been studied for such applications [6–8]. WO_3 revealed to be a good candidate for detection of different gases like H_2S [9,10], NH_3 [11] and H_2 [12], but most promising performances have been obtained for NO_2. Different preparation methods have been used to obtain films with different properties. Screen printing has been adopted by Chung et al. to deposit WO_3 thick films [13].

Thin films have been prepared by sputtering method obtaining NO_x sensors operating at 400 °C [14]. A detailed study of how deposition parameters affect the microstructure and the sensing performances of WO_3 sputtered thin films has been reported in [15]. Gas-sensing optimization has been highlighted to occur for a mean grain size value comparable with the depletion layer depth.

* Corresponding author. Tel.: +39 030 3715707; fax: +39 030 2091271.
E-mail address: ponzoni@tflab.ing.unibs.it (A. Ponzoni).

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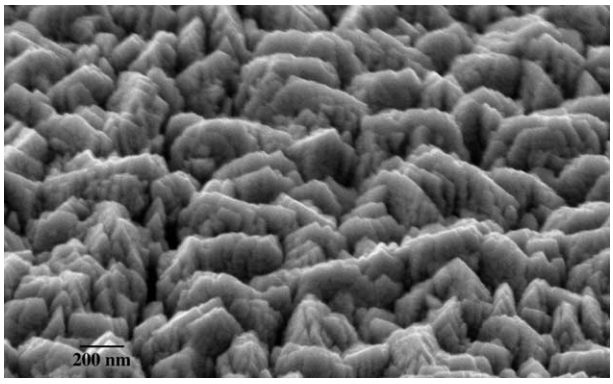

Fig. 1. SEM image of a WO_3 thin film deposited on Si/SiO_2 substrate.

Recently, Wang and co-workers reported about a nanocrystalline WO_3 film deposited by sol–gel that exhibit sub-ppm sensitivity towards NO_2 at 300 °C [16]. The high surface area offered by mesoporous layers and optimized grain size have been used to obtain a high sensitivity at the operating temperature of 36 °C [17]. Despite that several techniques have been explored to deposit films suitable for gas-sensing applications, less attention has been devoted to thermal evaporation. In this work, a modified thermal evaporation method has been used to deposit nanostructured WO_3 thin films with high surface roughness and large effective area. Sensing measurements carried out towards NO_2, CO and NH_3 at different temperatures ranging from 100 to 500 °C showed high responses and selectivity towards NO_2.

2. Experimental

Samples have been deposited by means of a modified thermal evaporation method on 3 mm × 3 mm × 0.25 mm substrates. Alumina ones have been used for the development of sensors while flat silicon ones covered by a thin layer of silicon dioxide have been used for the morphological characterization.

The source material was a metallic tungsten wire with basket shape (SPI Supplies Pk 10 1801). The chamber was evacuated with a rotary pump. The deposition process was carried out in a reactive atmosphere at constant pressure $p_{O2}=0.22$ mbar. A voltage of 5 V was applied to the W basket for 5 min resulting in an electrical current of about 10 A. Substrates were kept 15 mm above the target and heated at the constant temperature of 600 °C. After cooling, the substrates appeared to be covered with a light green film about 1.4 μm thick (measured with an Alphastep profiler).

For comparison, WO_3 thin films have been deposited on the same substrates by RF magnetron sputtering. The deposition has been performed starting from a metallic target with certified purity at 99.99% in an oxidizing atmosphere with 50% argon and 50% oxygen at a working pressure of 8×10^{-3} mbar. During the deposition process, the substrate was maintained at 300 °C to favour the formation of a stable layer. The deposition was carried out for 70 min resulting in a 300-nm-thick film. It underwent an annealing cycle at 500 °C for 12 h to enhance the stability of the film during the operation as gas sensor at lower temperatures. Annealing was performed in a furnace under controlled flux of humid synthetic air.

Layers deposited on alumina substrates were provided with interdigitated Pt contacts (IDC) for electrical measurements and with a Pt heater on the backside. Both Pt-structures have been deposited by means of DC magnetron sputtering.

The spacing period of the IDC structure is of 380 μm, with a distance between each "Pt finger" of 190 μm. SEM, TEM and an AFM were used for surface characterization. AFM measurements have been carried out with a Veeco CP-Research microscope in intermittent contact-mode (ic-mode). The tip was a Si one (NT-MDT, NSG10) with a 20-nm diameter and a 22° apex angle. TEM investigation was carried out with FEI Tecnai F20 microscope equipped with field emission source and operated at 200 keV. Bright field imaging has been used for specimen characterization.

The flow-through technique was used to test the gas-sensing properties of the thin films. A constant flux of synthetic air of 0.3 l/min with controlled relative humidity value (RH%) was the gas carrier, into which the desired concentration of pollutants – dispersed in synthetic air – was mixed. All the measurements were executed in a temperature-stabilised sealed chamber with 1 l volume at 20 °C. Electrical characterization was carried out by volt–amperometric technique; the sensor was biased by 1 V and film resistance was measured by a picoammeter, recording data every 20 s.

3. Results and discussion

3.1. Microstructure characterization

SEM characterization revealed that the film is composed of elongated agglomerates about 500 nm long. The deep holes that separate the elongated agglomerates give the

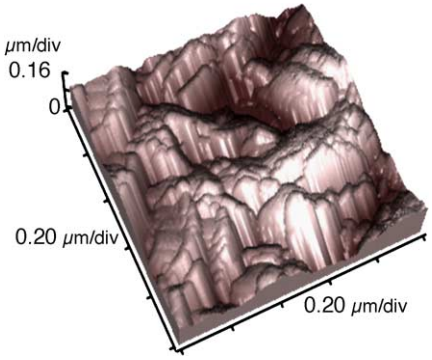

Fig. 2. 1 μm × 1 μm AFM image of a WO_3 film deposited on Si/SiO_2 substrate.