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Contributed Paper

Gas Sensing Properties of WO_3 Thin and Thick Films Prepared by Different Techniques

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ABSTRACT

Tungsten trioxide (WO_3) thin films are promising candidate sensing applications. This paper presents the sensing properties of WO_3 films prepared by different techniques, namely, r.f.. sputtering and precipitation technique. Attention has been focused on the influence on the preparation technique to the sensing properties of the material. All the films were deposited onto alumina substrates with fabricated Pt-film interdigital electrodes on front-side and a Pt-film heater on the back-side to perform electrical measurements in controlled atmosphere and temperature. The results showed that thin and thick films are very sensitive NO_2, the thin films are faster in response and recovery while the thick films have higher response value at lower operating temperatures.

1. INTRODUCTION

In the last decade the interest in the research of new gas sensing materials has grown, in order to achieve highly sensitive and selective long-term-operating sensors [1,2]. The production of materials with uninvestigated features is necessary for implementing electronic noses based on array of sensors and on signal processing tools.

Previous research has established that the WO_3 sensors prepared by spray-pyrolisis and firing on alumina tubes [3], sol-gel spin coating[4], vacuum thermal evaporation, VTE of pure WO_3 powder [5] and radio frequency sputtering RFS [6][7], are characterized by high sensitivity to sub-ppm levels of NO_x. The promising NO_2 sensitivity of WO_3 has recently led our research to the study of difference in sensitivities of WO_3 films prepared by thin and thick films technique.

Tungsten trioxide (WO_3) thin films are promising candidate sensing applications. This paper presents the sensing properties of WO_3 films prepared by different techniques, namely, r.f.. sputtering and precipitation technique. In this work attention has been focused on the influence on the preparation technique to the sensing properties of the material. Furthermore structural and micro-structural analyses of the films have been performed.

2. MATERIALS AND METHODS

Tungsten oxide thin films were prepared by reactive magnetron radio frequency 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 $8x10^{-3}$ mbar. During the deposition the substrate is maintained at 300°C to favor the formation of a stable layer and, after the deposition, the deposited layer underwent

an annealing cycle at 450°C for 12 hours to guarantee the stability of the films during the operation as gas sensor at lower temperatures. Annealing was performed in a furnace under controlled flux of humid synthetic air. WO_3 tends to suffer from exaggerated coalescence on annealing; therefore a moderately low annealing temperature was imparted. Temperature was measured by a thermo-couple placed on the internal wall of the furnace. For the electrical characterization, the films were deposited onto 3x3 mm^2 wide 250 μm thick Al_2O_3 substrates equipped with a Pt meander heater on the backside; Pt inter-digitated contacts were sputtered on the thin-film side for electrical measurements.

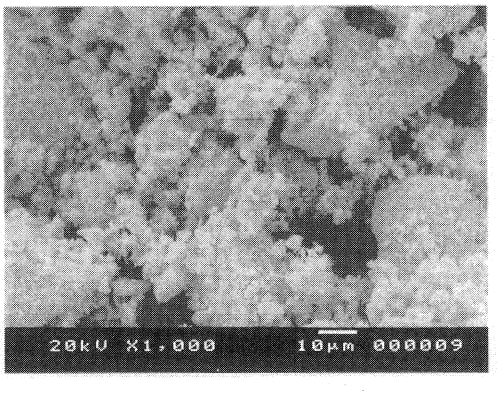
Thick films of tungsten oxide were synthesized by precipitation technique prepared using ammonium tungstate salt ($(NH_4)_{10}W_{12}O_{41} \bullet_5 H_2O$, Wako Chemical, Japan) and nitric acid (Carlo). Nitric acid solution was slowly dropped in the 80°C heated ammonium tungstate solution. The precipitated yellowish powder was separated using filter paper. The powder was heated at 200°C for 2 h to remove the water content and then calcined at temperature of 300-800°C for 2, 6 and 12 h. The deposition and annealing process strongly affects the microstructure, crystalline phase and chemical composition of the films. The deposition was performed on alumina 3x3 mm square substrates equipped with interdigitated contact on one side and the heater on the backside.

The flow-through technique was used to test the gas-sensing properties of the thin films. The gas carrier was a constant flux of synthetic air of 0.3 l/min into which the desired concentration of pollutants-dispersed in synthetic air-was mixed. All the measurements were executed in a temperature-stabilised sealed chamber at 20°C under controlled humidity. Electrical characterisation was carried out by volt-amperometric technique; the sensor was biased by 1 V and film resistance was measured by a picoammeter.

3. Results and Discussion

Figure 1 is a scanning electron microscope image showing surface morphology of the WO_3 powders calcined in air at 600 °C for 6 h. It shows very fine particles of the WO_3 - some of which formed agglomerates of ~30 μm in size. High magnification revealed that the agglomerates were made up of loosely pack 100-nm particles. A transmission electron microscope image (Figure 2) clearly shows the WO_3 particles of average size ~100 nm which is in good agreement with SEM observation. X-ray diffraction study (not shown) revealed monoclinic structure.

SEM images of a WO_3 film deposited via RF sputtering shows a compact and homogeneous morphology, possible thanks to the deposition technique that covers completely the alumina substrate. XRD analysis of RF sputtered thin film shows WO_3 tetragonal phase.



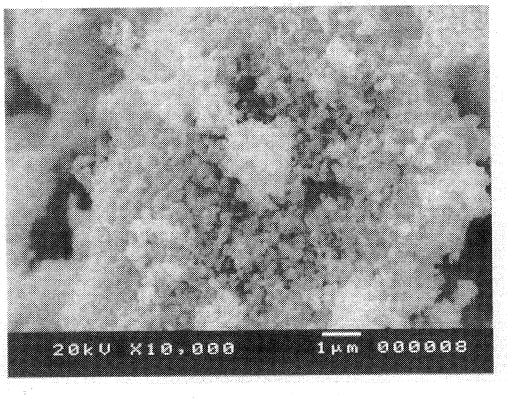


Figure 1. SEM pictures of the WO_3 powders used to fabricate thick film layer.

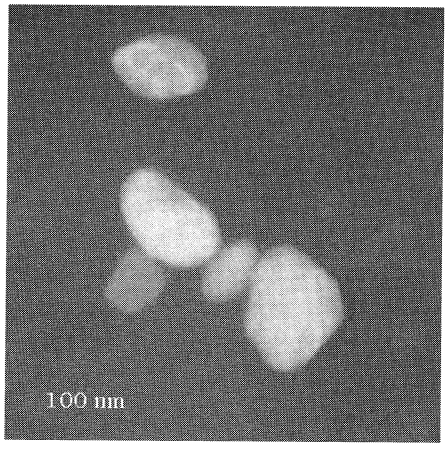


Figure 2. TEM picture of the WO_3 powders.

The conductance of the thin films layers is found to be between 10^{-6}-10^{-9} S when the films are operated in air with 50% RH and temperatures between 200°C and 450°C. This is a reasonable value for gas sensing applications. The gas sensing behavior of tungsten oxide thin and thick films were tested towards NO_2 at ppb levels in the temperature range between 200 and 450°C.

By defining G_f as the level of conductance when the pollutant is present and G_0 as the level in air, the response of the sensors toward NO_2 is defined as the ratio between the conductance in air and the conductance in presence of the gas for an n-type semiconductor, namely G_0/G_f.

The electrical behaviour of the thin films can be interpreted within the framework of the existing theory on chemical sensors. It is known in the literature that the resistance of semiconducting thin films is strongly influenced by the presence of oxidizing or reducing gases. The molecules of gas may interact with the surface of the semiconductor and then be adsorbed on it. There are two major categories for adsorption of a gas on a solid surface: physisorption and chemisorption. In the latter case the bonding is strong and, normally, the molecules dissociate into atoms while, in the former case, the bonding is weak and is usually associated with dipole-to-dipole interaction between adsorbate and adsorbent. At low temperatures the rate of chemisorption is so low that equilibrium cannot be reached in real time and thus the chemisorbed volume is low. Surface coverage by chemisorbed species first increases with temperature, until equilibrium state is reached, then starts to decrease because of desorption processes. Oxygen in the atmosphere is adsorbed on the surface of the semiconductor as different species (O_2, O_2^- and O^-). The adsorbate acts as a surface state by capturing electrons, which are held to the surface by electrostatic attraction; this mechanism causes the resistance of the films to grow in spite of a temperature increase.

Regarding NO_2 interaction with metal oxides, there are proofs of reactions directly with the semiconductor surface other than with the oxygen chemisorbed at surface. Tamaki *et al.* [9] studied nitrogen dioxide absorption on tin oxide surfaces by temperature programmed desorption measurements and found that the adsorbates originating from NO_2 are essentially the same as those for NO, since NO_2 molecule dissociate easily over the tin oxide surface. These results are in agreement with the work of Solymosi and Kiss who proposed the following reactions:

$$NO_g + e \rightarrow NO^-_{chem.}$$

$$NO_g \rightarrow NO^+_{chem.} + e$$

Where the second type of absorption is much weaker than the first one, Ghiotti *et*

al.[11] proposed similar reactions based on Fourier transform infrared spectroscopy measure-ments. The shape of the kinetic response can be explained by an increase in the height of the surface barriers at grain interfaces due to electron trapping in NO chemisorbed molecules.

Figure 3 reports the dynamical response of the sputtered thin films to concentration pulses of nitrogen dioxide in the ppb range at a working temperature of 300°C and with 50%RH. The conductance is decreasing as is normal for an n-semiconductor the response times are fast, lower than one minute, while recovery times are a little bit higher, between one and two minutes. The response to NO_2 introduction of the thick film layer is a decrease in the conductance too, kinetics is a little bit slower: response and recovery times are between 2 and 3 minutes.

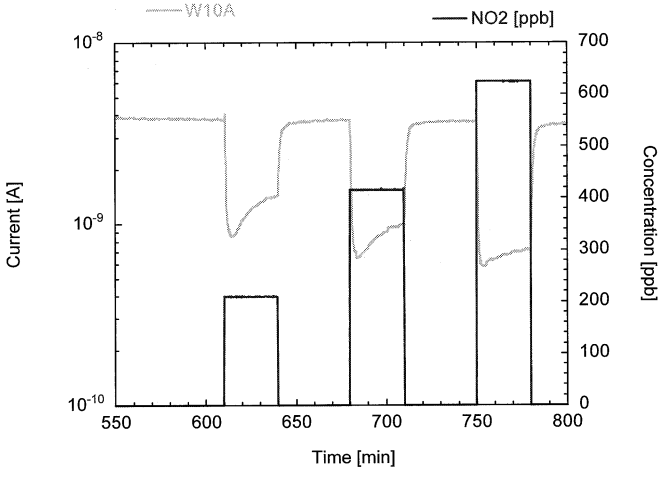


Figure 3. Current flowing through WO_3 thin film at 300°C as nitrogen dioxide pulses are introduced in the test chamber at 50%RH.

We can compare the response values at different temperatures looking at Figure 4 and Figure 5 that report the response as a function of nitrogen dioxide concentration at different working temperatures. The response of the thick film layer is higher compared to the thin film at a working temperature of 200°C, but at this temperature the recover of the conductance in air after the NO_2 introduction is not complete, therefore the response is not reproducible at this temperature, probably due to an irreversible adsorption of NO_2 on the semiconductor surface. The response of the thin film sensor was higher at higher temperature. While the response of the thick film sensor was higher at lower temperature. This may be due the difference in crystallite structure of the both sensors since the thin film sensor was tetragonal and the thick film one was monoclinic.

4. CONCLUSIONS

WO_3 thin and thick films were prepared by r.f. sputtering and precipitaition. The films show potential application for the measurement of nitrogen dioxide in the ppb concentration range. Thick films have shown greater response at 200°C with respect to sputtered films, but this operating temperature correspond to a partially irreversible absorption of nitrogen dioxide on the thick film surface leading to an irreversible change in the conductance. At higher temperatures the response of the thin film is slightly higher. Thin films are slightly faster than thick films.

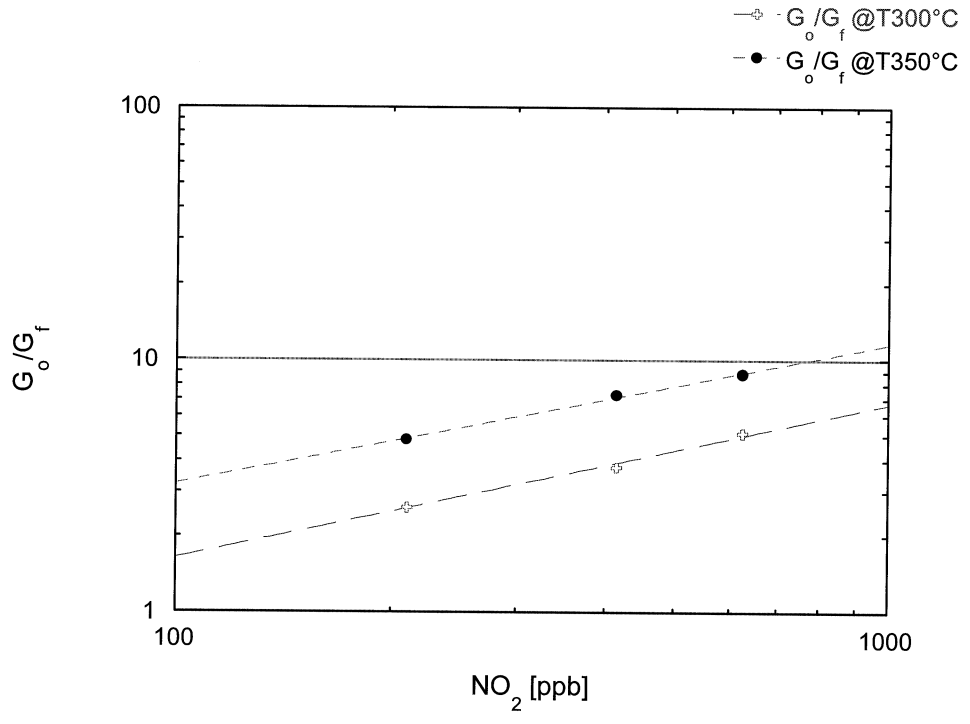


Figure 4. Response of WO_3 thin films as a function of nitrogen dioxide concentration at the ppb level.

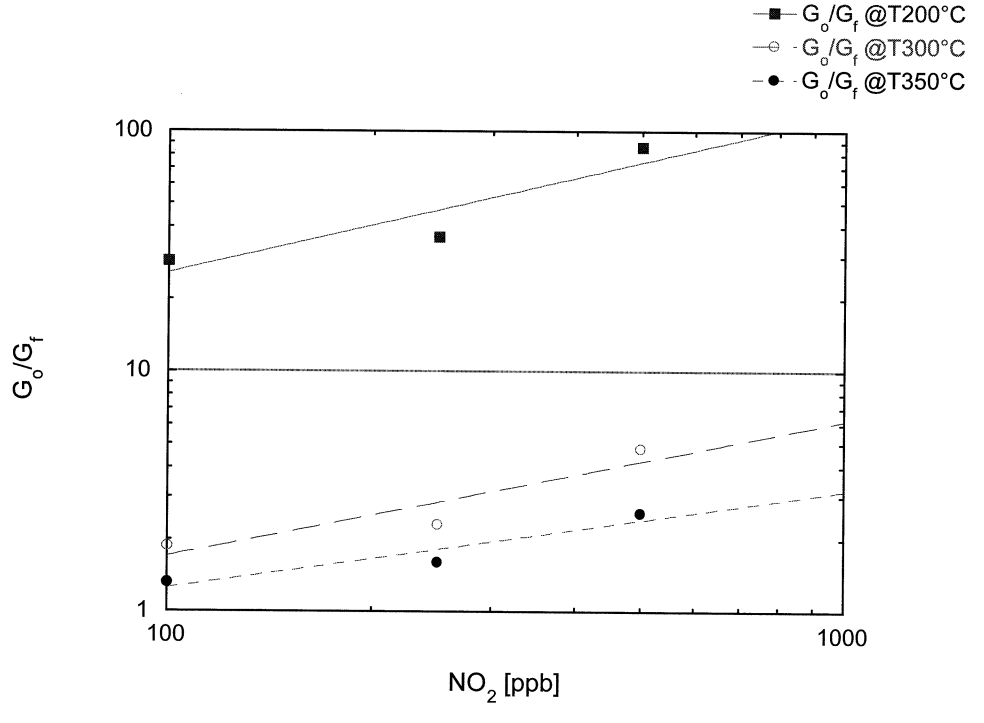


Figure 5. Response of WO_3 thick films as a function of nitrogen dioxide concentration at the ppb level.

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