MICROMACHINED HYDROGEN SENSORS WITH NANOSTRUCTURED TUNGSTEN OXIDE ACTIVE LAYERS: NANODOTS VS NANOTUBES. A COMPARATIVE STUDY

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Abstract

Nanostructured metal oxides are of growing importance for application as active layers in gas micro-sensors. Tungsten trioxide is the most promising candidate for selectively detecting hydrogen, which is an important issue in hydrogen-energy-based systems for safety use.

In this work, two types of sensors employing identical silicon micro-hotplate transducer geometry but with different morphological structures of the active film are prepared and evaluated. Type 1 sensor utilizes a smooth thin film composed of self-ordered tungsten oxide nanodots synthesized by anodizing Al/W/Ti metal layers, whereas Type 2 sensor employs an array of tungsten oxide nanotubes prepared by sputter-deposition over porous anodic alumina templates.

While Type 1 sensor is considered as mainly two-dimensional limiting the response kinetics to the sensitive film surface, Type 2 sensor is three-dimensional since the diffusion of chemical species within the nanotubes and their interaction with the nanotube walls play an important role in the detection mechanism.

The dataset for each micro-sensor comprised hydrogen dosed with various concentrations at several operating temperatures. The results show, for example, that the sensitivity of Type 2 sensor is tenfold higher whereas Type 1 sensor is 5 times faster, both being best responsive to hydrogen gas at as low temperature as 150\textdegree C. Although the two sensing films were successfully integrated in the micro-hotplate transducers, the approach to forming Type 1 sensor is more facile, cost-effective, better reproducible and reduces the number of processes, materials and production time.

Keywords: WO\textsubscript{3} nanodots, anodizing, nanoporous alumina, sputtering deposition, hydrogen detection

1. INTRODUCTION

The use of gas sensors based on nanostructured metal oxides has emerged as one of the most important research topics in sensors. It is known that a reduction in the materials grain size remarkably enhances the features of the materials [1, 2]. The extremely small grain size in such materials provides a very large surface area for interaction between the metal oxide and the analyte to be detected. During the last years, various ways to increase the surface of sensor active layers have been reported. In this work we present the preparation of two types of nanostructured active layers of metal oxide sensors with substantially enlarged surface-to-volume ratios - porous-alumina-assisted tungsten oxide nanodot film and porous-anodic-alumina-supported nanotubular tungsten oxide layers – and report on the comparative analysis of their properties for hydrogen detection.
2. EXPERIMENTAL

The basic structure of gas sensing devices fabricated in this work consists of a micro-hotplate type substrate comprising a silicon nitride membrane, a heating poly-silicon meander, an insulating layer, a gas sensitive material and a pair of interdigitated electrodes for measuring the film resistance.

![SEM image of a 4-element microsensor chip and optical microscope images of a single sensor element and a 4-element microsensor assembled in a standard TO-8 package.]

Microsensors were fabricated using a four-inch p-type Si wafer, with (100) crystal orientation and 300 µm in thickness. A 300 nm thick Si₃N₄ layer was grown by low-pressure chemical vapor deposition (LPCVD) on both wafer sides. Micro-heaters, 250 nm thick, made of POCl₃-doped polysilicon layer were then patterned on the face wafer side. An 800 nm thick SiO₂ layer was grown to electrically isolate the heaters from the active layers to be prepared later.

The two different fabrication approaches that had been developed for sensing layers are elaborated in the text below and sketched in the Figure 2.

![Schematic layout of the fabrication process for porous-alumina-assisted tungsten oxide nanodot film (Type 1 sensor) and porous-anodic-alumina-supported nanotubular tungsten oxide layers (Type 2 sensor) on micro-hotplate transducers.]

**Fig. 1.** a) SEM image of a 4-element microsensor chip and optical microscope images of a) a single sensor element and c) a 4-element microsensor assembled in a standard TO-8 package.

**Fig. 2.** Schematic layout of the fabrication process for porous-alumina-assisted tungsten oxide nanodot film (Type 1 sensor) and porous-anodic-alumina-supported nanotubular tungsten oxide layers (Type 2 sensor) on micro-hotplate transducers.
2.1. Type 1 sensor fabrication

900 x 900 μm squares (future areas of gas sensing layers) were defined as with a photolithographic step over a preformed micro-hotplate (Fig. 2a, left). A 20 nm thick titanium adhesive layer, 50 nm thick tungsten layer and 400 nm aluminium layer were successively deposited by radio frequency (RF) magnetron sputtering over the patterned photoresist (Fig. 2b, left). The Al/W/Ti multilayers were anodized in a two-electrode cell made of polytetrafluoroethylene using a two-step anodising process [3]. The first anodising step was performed with an aqueous solution of 0.4 mol dm⁻³ H₂C₂O₄ and the addition of 2.4 mmol dm⁻³ NH₄F [4] by applying a constant voltage of 27 V resulting in growth of a nanoporous alumina layer (Fig. 2c, left). When the alumina barrier layer reached the tungsten film, nuclei of anodic tungsten oxide (nanodots) were formed at the Al₂O₃/W interface (Fig. 2d, left). A reanodization process was carried out in the same electrolyte by sweeping the voltage from 27 to 100 V in order to improve the homogeneity of the tungsten oxide nanodots and completely oxidize the remaining tungsten and titanium metals (Fig. 2e, left).

After completing the anodization process, the photoresist with the anodized metals on it was removed by a lift-off process (Fig. 2f, left). Then the nanoporous alumina overlay was selectively etched away by dipping the wafer in a CrO₃ : H₃PO₄ solution kept at 60 °C. The wafers were subsequently annealed at 500°C during 2 h in order to crystallize the tungsten oxide nanodots. After opening contact microholes in the SiO₂ layer to the heater ends, pairs of platinum interdigitated electrodes (with 50 μm interline gap) were placed over the nanodot film (Fig. 2g, left). Backside silicon etching with KOH kept at 70°C was performed to create the thermally insulated membranes. The fabrication process ended with wafer dicing and assembling the sensor chips on a standard TO-8 package using ultrasonic wire bonding.

2.2. Type 2 sensor fabrication

After patterning a photoresist for defining the sensor active areas as described above, a 40 nm thick titanium layer and 380 nm thick aluminium layers were deposited by RF magnetron sputtering (Fig. 2b, right). The anodizing process was carried out in two steps. At the first step, a half of the aluminum layer was potentiodynamically anodized at 210 V, and was then selectively dissolved away. The second anodizing was performed at a constant current density of 8 mA cm⁻², until the aluminum metal was oxidized down to the aluminum underlayer with the formation of low aspect ratio porous alumina film (Fig. 2c, right), which will be used as support for further deposition of WO₃ layer.

Following anodizing, a lift-off process was performed to leave the porous alumina within the active areas only (Fig. 2d, right). The remaining nanoporous alumina layer was partially etched with a mixture of phosphoric and chromic acid solution to increase the diameters of the pores (Fig. 2d, right). Then areas of 250 nm thick layer of tungsten trioxide were prepared over the porous alumina squares by magnetron sputtering and a lift-off process (Fig. 2e, right). After that microholes to contact the heater ends were opened in the SiO₂ layer and pairs of platinum electrodes were prepared over the sensing layer. The thermal treatment (after the deposition of WO₃ layer), electrode formation, micromachining of the bulk silicon, dicing and packaging the chips were performed in the same way as for Type 1 sensors.

2.3. Film characterization and gas sensing test

Morphological and structural characterization of the gas sensing layers were performed by field emission scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) with sectioning by focused ion beam (FIB), atomic force microscopy (AFM), energy dispersive X-ray (EDX) analysis and X-ray diffraction (XRD).

A fully-automated experimental set-up was developed and employed for gas sensing characterization. The desired concentration of hydrogen was obtained using a mass-flow controlled system. The total gas flow was 100 ml min⁻¹. The sensor response was monitored using a 6517A model Keithley equipment and controlled by a LabView program. A constant voltage was applied to the heating elements to set the operating temperature of the sensors.
3. RESULTS

Fig. 3 shows SEM views of fragments of the active layers of Type 1 and Type 2 sensors. While the sensing film of Type 1 sensor basically consists of a two-dimensional self-ordered arrangement of tungsten oxide nanodots, the film of Type 2 sensor is composed of a three-dimensional arrangement of metal-oxide nanotubes. The nanodots are ~50 nm in diameter and are distributed with the average center-to-center distance of 65 nm. In the sensing film of sensor Type 2, the diameter of the tubes and their depth are estimated to be ~262 and ~140 nm respectively. The mean grain size in the sputtered WO$_3$ layer was 24 nm while the average grain size in the WO$_3$ nanodot film was found to be about 9 nm. The SEM images in Fig. 3c and d) show that the clogging of the nanopores was avoided, a noteworthy feature from the point of view of the gas sensing application, as it would allow analytes to diffuse into pore openings and to come in contact with the active film providing a very high surface of interaction.

![SEM images of fragments of the gas-sensing film of (a,b) Type 1 sensor and (c,d) Type 2 sensor, prepared as in Fig. 2 and 3 respectively](image)

The crystalline structure of the annealed anodic films was determined by XRD. The results revealed the presence of monoclinic WO$_3$ phase in the porous-alumina-supported tungsten oxide layer while the annealed self-organized tungsten oxide nanodot film appeared to be composed of another polymorph in the tungsten oxide system - monoclinic WO$_3$.

![Sensor response of (left) Type 2 nanodot sensor and (right) Type 1 nanotub sensor to 1000 ppm H$_2$ at an operating temperature of 250ºC.](image)

Fig. 4 shows the response of the two sensor types to 1000 ppm hydrogen at 250ºC of operating temperature. The difference in the initial film resistance between the sensors may result from the different film thicknesses arisen from the features of the film formation techniques.
Fig. 5. Temperature-dependent responses to 1000 ppm H₂ of Type 1 and Type 2 sensors. The response is the sensor resistance in the gas over the resistance in dry air.

Sensor response was calculated as the baseline sensor resistance in dry air \( (R_{\text{air}}) \) divided by the sensor resistance in the presence of hydrogen gas \( (R_{\text{gas}}) \). For both sensor types, the maximum response was obtained at a low operating temperature of 150°C. However, the response of Type 2 sensor (1350) appeared to be by order of magnitude higher than that for Type 1 sensor (130). The difference in sensitivity between the sensors could be explained by the differences in film morphologies and structural characteristics, leading to dissimilar kinetics of surface interaction with the gas. Likely, in the case of the WO₃ nanotubes, the higher surface area contacting the gas results in a higher sensitivity. As the sensor response is also related to the thickness of the active layer, one may expect that the sensor sensitivity would increase, at least to some extent, for a relatively thicker film because of the increased volume of interaction. Possibly, the sensitivity of Type 1 sensor may be improved by growing the film on substrate having preformed morphology at the microscale. The grain size of the WO₃ films and their crystalline structure may also influence the response kinetics and affect the film sensitivity.

Fig. 6. Response and recovery time determined for Type 1 and Type 2 sensors to 1000 ppm H₂ as a function of operating temperature.
Fig. 6 shows temperature-dependent response and recovery times for the two sensor types. These parameters are defined as the time necessary to reach 90% of the final response value after the gas is added or removed from the chamber. For the two sensor types, the response and recovery time shortens when the operating temperature is increased due to faster kinetic reactions at elevated temperatures. However, the nanotube sensor was significantly slower than the nanodot sensor, which suggests that the diffusion of the gas species into the tungsten oxide coating the pores of the alumina nanotemplate plays an important role in response kinetics [5]. The faster response and recovery time for Type 1 sensor could be also due to a smaller grain size and thinner film thickness, both speeding up the diffusion of analyte species within the film and making it readily reversible.

4. CONCLUSIONS
Two types of nanostructured tungsten trioxide gas sensing films and relevant micro-sensors have been prepared and evaluated. Type 1 sensor utilized a smooth thin film composed of self-ordered tungsten oxide nanodots synthesized by anodization of Al/W/Ti metal layers, whereas Type 2 sensor employed an array of tungsten oxide nanotubes prepared by sputter-deposition over the porous anodic alumina template. While Type 1 sensor can be considered as mainly 2-dimensional, Type 2 sensor is 3-dimensional since the diffusion of the different chemical species within the nanotubes and the interaction of diffusing molecules.

For both sensor types, the maximum response was obtained at a low operating temperature of 150ºC. The difference was that the response of Type 2 sensor was by order of magnitude higher than that for Type 1 sensor. We believe that the higher response for Type 2 sensor is mainly due to the higher surface interaction with the analyte. On the other hand, the response and recovery time for Type 1 sensor were respectively 5 and 50 times faster at the best operating temperature.

The two sensing films were successfully integrated in the micro-hotplate transducers. The approach to forming Type 1 sensor has proved to be more facile, cost-effective, better reproducible and cut off the number of processes, materials and fabrication time.

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LITERATURE