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Tungsten Oxide Nanowires on micro hotplates for Gas Sensing applications

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Abstract

Tungsten oxide nanowires (NWs) were successfully deposited on the membrane of micro hotplates (ams, Germany) by a very simple and scalable thermal oxidation technique. Synthetized nanostructures were morphologically investigated by mean of a FE-SEM (LEO 1525) and the structure was analysed by X-Ray Diffraction and Raman Spectroscopy. Micro hotplates were mounted on standard TO packages by gold wires by electro soldering in order to fabricate a batch of sensing devices.
The performances of the fabricated devices were tested towards some chemical compounds of interest (NO_2, Acetone, Ethanol and CO). Firstly a temperature screening was performed, to identify the optimal working temperature in presence of each target compound. Moreover, calibration curves were obtained, and the influence of humidity was taken into account for NO2.

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Keywords: metal oxides nanowires; micro hotplates, chemical sensing

1. Introduction

Metal oxides (MOX) are among the most common materials being used for gas sensing applications due to their high stability, low cost and good sensitivity compared with most of the other gas sensing materials. Metal oxide

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nanowires, in particular, are well-known as candidate for a new generation of low-cost chemical sensors. Nanostructured tungsten oxide could enhance the overall performances of the devices compared to traditional thin film technology [1][2]. As widely known, metal oxide sensing mechanism is thermally activated, and the optimal working temperature is in the range of 200-400°C [3]. Power consumption of the whole device is thus a limiting factor for their use in a wide range of applications.

Micro hotplates integrate both electrodes and heating elements on a micro-fabricated (MEMS) membrane. In particular, ams is a leading company in the field of gas sensor devices, and its family of micro hotplates provided very low power consumption together with the ability to sustain high working temperature (max 550°C) (Figure 1).

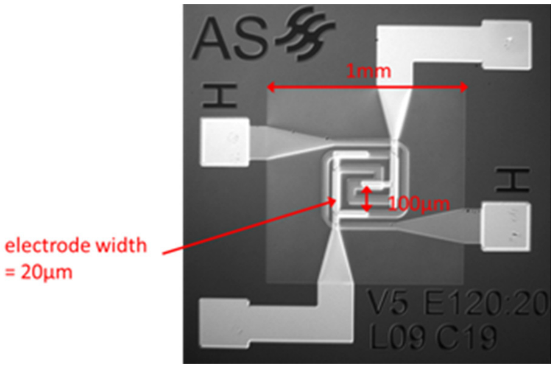

Figure 1: ams micro hotplate model E120:20.

2. Experimental

Thermally oxidized tungsten oxide nanowires were successfully synthetized on ams E120:20 micro hotplates, using a tubular furnace in low vacuum. A thin layer (100nm) of metallic tungsten was deposited on the hotplates by RF magnetron sputtering (100 W argon plasma, $5.5x10^{-3}$ mbar, room temperature). Afterwards, samples were oxidized in a tubular furnace at 600°C for one hour, in order to promote the growth of the nanowires. Pressure inside the alumina tube was set at 0.8 mbar, with an argon flow of 10 SCCM.

A field-emission scanning electron microscope (FE-SEM) LEO 1525 was operated at 3-5kV, in order to investigate the morphology of the nanostructures.

Raman spectra were measured by HORIBA monochromator iHR320 configured with a grating of 1800 g/mm, coupled to a Peltier-cooled Synapse CCD. A He-Cd laser (442 nm) was focused on the samples by a fiber coupled confocal optical microscope (HORIBA) at 100x magnification. Spectra were recorded in the wavelength range 200-1200 cm^{-1}.

In order to fabricate the soldering pads for the sensing devices, we firstly deposited a TiW adhesion layer by DC magnetron sputtering (70 W argon plasma, 300 °C, $5.5x10^{-3}$ mbar), and then we deposited interdigited platinum contacts, using the same condition described before. A platinum heater was deposited on the back-side of alumina substrates via the same two-steps technique used for contacts. Samples were finally mounted on TO packages using electro soldered gold wires.

Functional characterization was performed on the fabricated devices. Optimal working temperature towards some chemical compound of interest was identified. In particular, nitrogen dioxide, carbon monoxide, ethanol and acetone were selected as target compounds. The influence of humidity was also taken into account.

3. Results

Figure 2 shows a SEM picture of tungsten oxide nanowires obtained on ams micro-hotplates. Nanowire diameters were estimated in the order of few tens of nanometers (20-30nm).

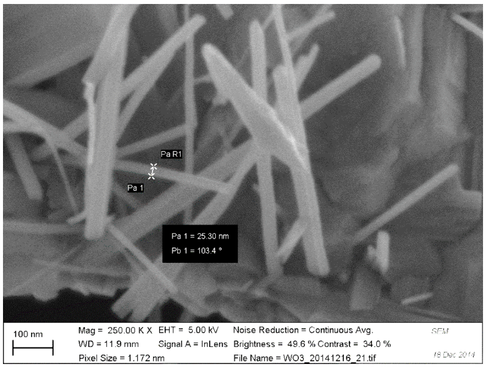

Figure 2: SEM picture of WO_3 nanostructures synthetized on ams substrates, at 600°C with a pressure of 1 mbar (60 minutes).

Structural investigation confirms the crystallinity of the material, resulting in pure tungsten trioxide (Figure 3). The recorded spectrum perfectly matches the WO_3 reference [3]: 798 cm^{-1} and 705 cm^{-1} peaks are typical Raman peaks of monoclinic crystalline WO_3 (W-O-W stretching vibrations). The additional peaks at 264 and 321 cm^{-1} are due to the bending vibration δ(O-W-O).

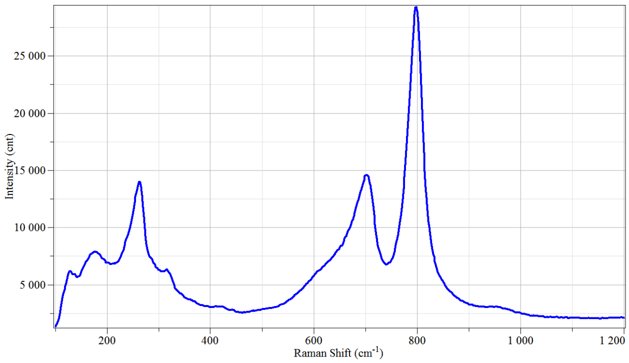

Figure 3: Raman Spectroscopy of WO_3 nanostructures synthetized on alumina substrates, at 600°C with a pressure of 1 mbar (60 minutes).

Functional characterization was performed on the fabricated devices. Dynamic response shows the typical behavior of n-type tungsten oxide in presence of oxidizing (NO_2) and reducing (ethanol, carbon monoxide and acetone) gases (Figure 4, left). Optimal working temperature results 400°C for ethanol and acetone, and 200°C for nitrogen dioxide. Calibration curves were performed at these temperatures, and power law fitting were calculated (Figure 4, right). Detection limits, defined as the gas concentration to have a response of one, were estimated as 6 ppm for ethanol and acetone, and 0.1 ppm for nitrogen dioxide.

Repeatability of the measure was also investigated, resulting in a mismatch of less than 20% over three consecutive measurements. The influence of humidity was also taken into account. Investigation confirms that changing the humidity from 20% to 80% has less influence on the measure than repeatability itself.

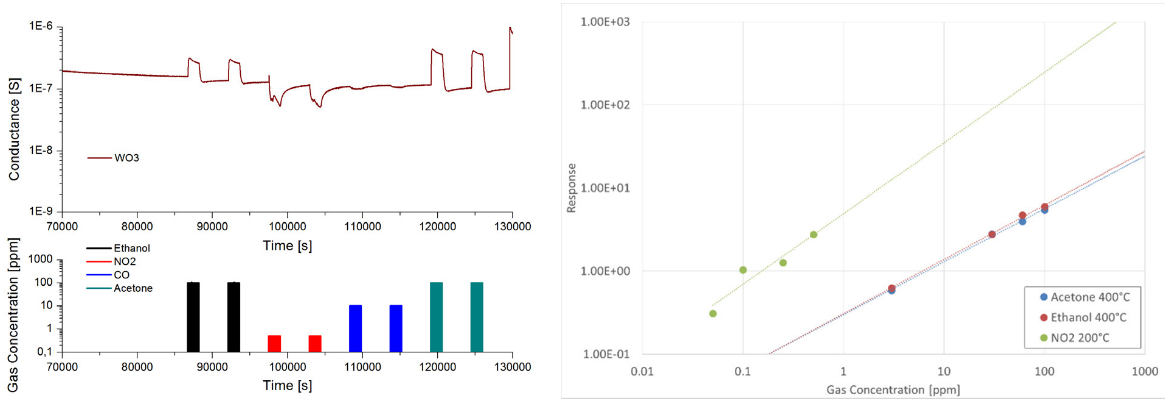

Figure 4: (left) Dynamic response of WO_3 NWs on ams micro hotplate model E120:20 at 200°C, with RH=50%@20°C. (right) Calibration curve and power fitting of WO_3 NWs on ams micro hotplate model E120:20 with RH=50%@20°C.

4. Conclusions

Tungsten oxide nanowires were directly grown on ams micro hotplate by using thermal oxidation technique in vacuum. Investigation confirms the crystalline structure of the material, and the low dimensionality. Conductometric chemical sensing devices were fabricated, and the functional performances were evaluated in presence of some chemical compounds.

In conclusion, the use of micro hotplates devices is compatible with this synthesis technique, and enable the fabrication of low power devices for a completely new range of applications.

Acknowledgements

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References

[1] Wang, X.S., Miura, N. and Yamazoe, N., Sens. Actuator B-Chem. 2000, 66(1-3), 74
[2] Meng, D., Shaalan, N.M., Yamazaki, T. and Kikuta, T., Sens. Actuator B-Chem. 2012, 169, 113
[3] Zappa D., Bertuna A., Comini E., Molinari M., Poli N., Sberveglieri G., Anal. Methods, 2015, 7, 2203–2209