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Niobium oxide nanostructures for chemical sensing

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Abstract

Niobium oxide nanostructures were synthesized by hydrothermal method starting from niobium films deposited by RF magnetron sputtering on 2×2 mm^2 alumina substrates. The samples were firstly treated with a KOH solution and with HNO_3, and then annealed to obtain the Nb_2O_5 nanostructures. A scanning electron microscope (SEM) was used to investigate the morphology of the samples, while RAMAN spectroscopy was used to analyse their structural properties. In order to study the functional properties of the material, electrical contacts and heating elements were deposited over the substrates by DC magnetron sputtering. The as-prepared samples were mounted on TO packages using gold wires. Afterwards, functional tests were performed in a test chamber to investigate their electrical conductance variation as a function of the surrounding atmosphere and thus the sensitivity to different gaseous species.

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Keywords: Niobium Oxide; Nanostructures; Hydrothrmal Method; Chemical Sensing; Raman Spectroscopy

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1. Introduction

Gas sensors based on nanostructures of metal oxide are widely studied in the literature [1] for their high sensitivity to different gaseous species. The reduced size of the sensors allows the realization of integrated devices to detect the presence of toxic gases. The hydrothermal treatment of a niobium foil is one of the first methods proposed in literature [2] to fabricate niobium oxide nanostructures. However, the obtained nanostructures must be removed from the foil and placed on a substrate to realize the sensor. On the contrary, in this work nanostructures are directly grown on the active transducer.

2. Experimental

2.1. Preparation of substrates

The preparation of samples started with the cleaning of alumina substrates to remove deposited particles and organic compounds. In particular, the cleaning was carried out in acetone with ultrasonic cleaner for 15 min and finally a flow of synthetic air was used to dry the samples to avoid the formation of halos. Afterwards, niobium films with a thickness of approximately 3 μm were deposited by RF magnetron sputtering on one side of alumina substrates. To obtain samples with these characteristics the deposition time was 5 h and 50 at 400°C. Furthermore, the power applied to the target was of 100 W, the argon flow was of 7 sccm and the pressure inside the chamber was of $5.3 \cdot 10^{-3}$ mbar.

2.2. Hydrothermal treatment

The nanostructures were obtained by placing the samples in an autoclave with 8 mL of 0.02 M KOH solution for about 15 h and the working temperature was of 170 °C. After the hydrothermal treatment a white compound covered all the surface of the samples. The as-prepared samples were subjected to a treatment with HNO_3 and to an annealing at 650 °C under argon flow to obtain the niobium oxide nanostructures [2].

2.3. Morphological and structural analysis

To ascertain the presence of the nanostructures the morphology of the samples was analyzed by a field emission scanning electron microscope (FE-SEM) LEO 1525. The good quality of the observation has been guaranteed by the presence of a carbon-based glue that reduced the sample charging.

Raman spectroscopy has been used in order to validate the presence of niobium oxide. A HORIBA monochromator iHR320, a Peltier-cooled Synapse CCD, a He-Cd laser (442 nm) and a fibre-coupled confocal optical microscope (HORIBA) composed the system for Raman spectroscopy.

2.4. Gas Sensing

The sensitivity of the samples was tested by measuring the resistance-conductance variation due to exposure to different gaseous species. To do this, it was necessary to deposit contacts on the niobium oxide to measure the variation of current. On the other side of the alumina substrates a heating element was deposited to study the behavior of the sensors at different working temperatures. To deposit contacts and heating element the DC magnetron sputtering technique was used. Gold wires were used to connect the samples on TO packages.

The sensors were placed in a test chamber to investigate their functional properties in response to different gases in a wide range of working temperatures (300-600 °C). The total flow inside the chamber was 200 sccm and was constituted by synthetic air mixed, from time to time, with the gaseous species of interest in different concentrations. Measurements were obtained by keeping the climatic chamber at 20 ° C, with a relative humidity equal to 50% and applying 1V to the devices [3].

3. Results

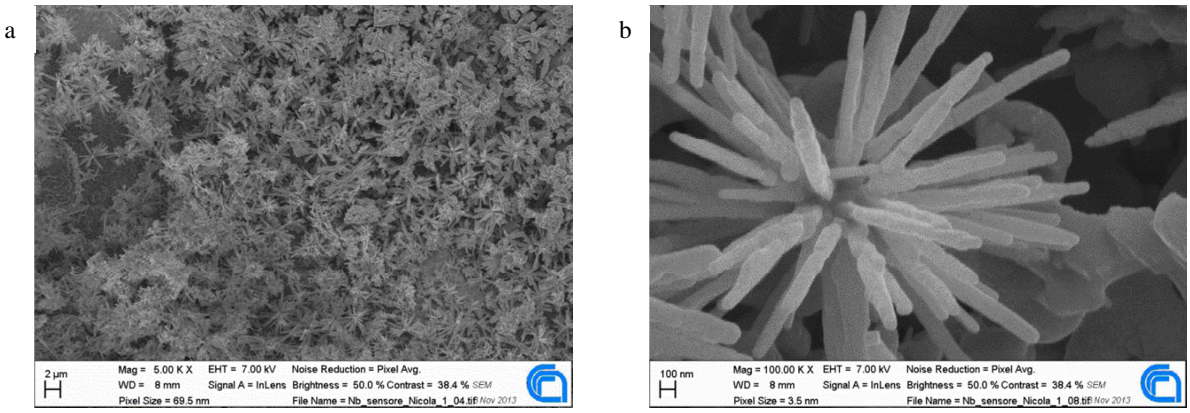

Fig. 1. (a) SEM pictures of prepared nanostructures at 5K magnification level; (b) 100k magnification level.

The surface of the samples was investigated by SEM after the hydrothermal treatment to verify that the nanostructures were grown. Figure 1 shows the morphology of the samples. Afterwards, the samples were subjected to Raman spectroscopy to ascertain the presence of niobium oxide. Measurements confirmed the presence of Nb_2O_5 nanostructures and showed $K_4Nb_6O_{17}$ residual after 24 h of HNO_3 treatment and the annealing at 650 °C (Fig.2).

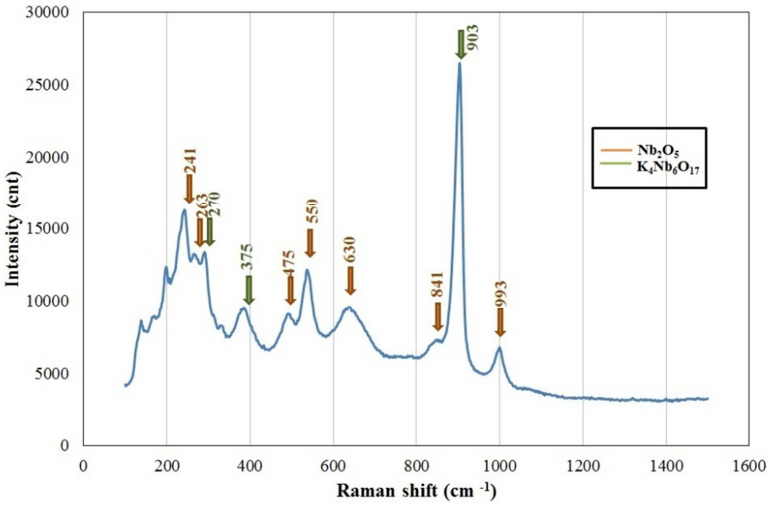

Fig. 2. RAMAN spectrum of prepared nanostructures

The sensitivity of the devices was tested to hydrogen in different concentrations and at different working temperatures (300-600 °C). Fig. 3 shows the dynamic response of the sensors to hydrogen at 500 °C (a) and their sensitivity to 200 ppm of H_2 in the entire range of temperatures (b).

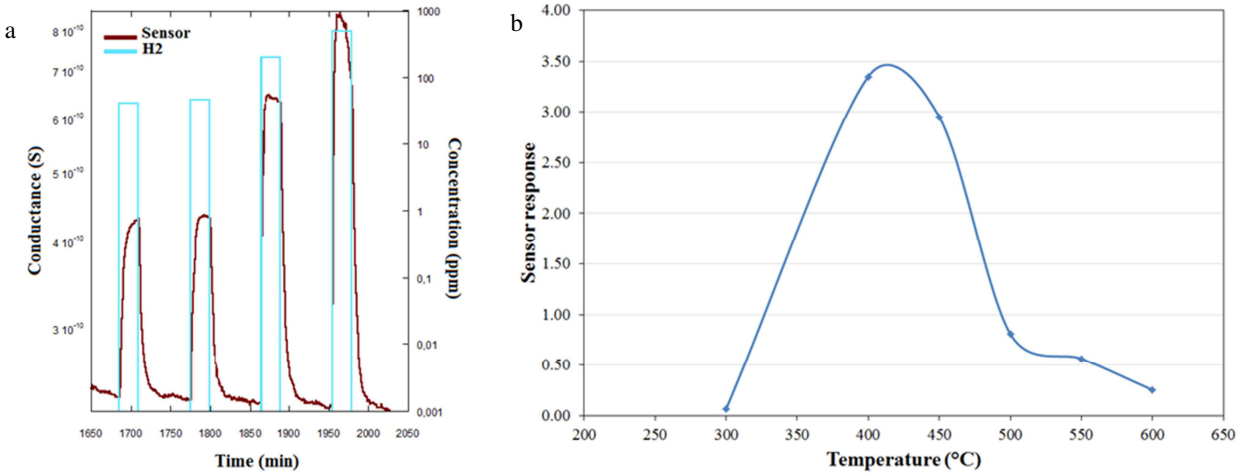

Fig. 3. (a) Dynamic response of prepared nanostructured to H_2 @500 °C with RH=50%@20°C; (b) Response of prepared nanostructures at different temperatures to 200 ppm of H_2

4. Conclusions

Niobium oxide nanostructures were grown directly on the active transducers by using the hydrothermal treatment. The sensitivity of the devices was tested to different concentration of hydrogen and at different working temperatures. The optimum was found at 400 ° C for a gas concentration of 200 ppm with a relative humidity of 50%. Thanks to this promising result, the sensitivity of the sensors will be evaluated towards other gaseous species.

Acknowledgements

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References

[1] M. Tonezzer, S. Iannotta, *H_2 sensing properties of two-dimensional zinc oxide nanostructures,* Talanta, 122 (2014) 201-208

[2] X. Fang, L. Hu, K. Huo, B. Gao, L. Zhao, M. Liao, P. K. Chu, Y. Bando, D. Golberg, *New Ultraviolet Photodetector Based on Individual Nb_2O_5 Nanobelts,* Adv. Funct. Mater. 21 (2011) 3907-3915

[3] D. Zappa, E. Comini, G. Sberveglieri, *Gas-sensing properties of thermally-oxidized metal oxide nanowires,* Procedia Eng. 47 (2012) 430-433