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Influence of Nb-doping on hydrogen sensing performance of WO_3 nanowires

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Abstract

Tungsten oxide nanowires were synthetized by thermal oxidation in vacuum, using a custom tubular furnace, adding niobium in the growth process to evaluate the influence of niobium in the conductometric response towards hydrogen gas.
Samples were characterized by XRD and Raman spectroscopy, to confirm the crystalline structure of the material.
The conductometric response of fabricated sensors was evaluated towards hydrogen gas. The addition of small percentage of niobium during the synthesis enhance the hydrogen sensing performance of the devices.

Keywords: Metal oxide nanowires; chemical sensors; tungsten trioxide; niobium

1. Introduction

Hydrogen is a tasteless, odorless and colorless gas that is quite difficult to detect with human senses, and even with standard scientific techniques. It is highly flammable: in air flammability limits are from 4% to 75% in volume, reaching 94% in oxygen mixture. Due to popular demand of hydrogen in industrial applications, like for example fuel cells, accurate detection and monitoring is required for hydrogen production and storage [1].

Metal oxides materials show properties covering almost all aspects of material science and physics in areas including electronics, superconductivity, ferroelectricity, magnetism. Among those, metal oxides are already established in the field of gas sensing. Metal oxide nanostructures combine the advantages of oxide materials with improved performance due to nanoscale dimensions. In particular, the downsizing of sensing materials and the high surface-to-volume ratio improve sensor performance. Moreover, high degree of crystalline order enhances long-term stability.

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In this work, tungsten oxide nanowires were synthetized by thermal oxidation in vacuum, using a custom tubular furnace, adding niobium in the growth process to evaluate the influence of niobium in the conductometric response towards hydrogen gas.

2. Experimental

Thin tungsten layers were deposited on alumina substrates via RF magnetron sputtering, and then oxidized at 600°C in furnace at 1mbar pressure. Moreover, small percentage of niobium was added to tungsten films, by adding some niobium stubs (12) at the metal target during sputtering process. Samples underwent the same oxidation process as bulk tungsten films.

Electron microscopy (FE-SEM) was use to characterize the morphology of nanowires, while X-Ray Diffraction and Raman spectroscopy were performed on samples to confirm the structure of the nanostructures.

Conductometric sensing devices were fabricated by depositing platinum contacts on top of nanowires by magnetron sputtering, and a platinum heater on the backside of alumina substrates [2]. Samples were mounted on TO cases by electro-soldered gold wires.

Performance of devices were evaluated towards hydrogen using flow-meter technique. In particular, working temperature of sensors was tuned to identify the optimal one for hydrogen detection. Moreover, calibration curves were measured, for both bulk and Nb-added tungsten trioxide samples.

3. Results and Conclusions

In Fig. 1 are reported SEM pictures of both bulk (left) and Nb-doped (right) WO_3 nanowires. The addition of niobium to the tungsten layer does not affect significantly the morphology of the synthetized nanowires, which exhibit diameters of few tens of nanometers.

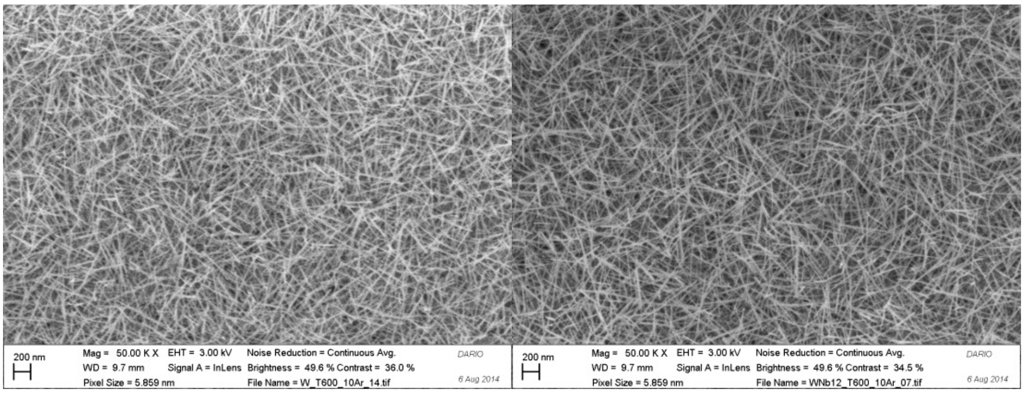

Fig. 1. (left) bulk WO_3 nanowires; (right) Nb-doped WO_3 nanowires.

Energy Dispersive X-ray Analysis (EDX) performed on metal layers prior to oxidation resulted in about 9.5% of atomic niobium in tungsten on the substrates (Fig. 2, left). Both XRD and Raman spectroscopy confirm the crystalline structure of the material, as reported in Fig. 2 (right), resulting in standard monoclinic crystalline WO_3. There is no experimental evidence of a secondary or a mixed phase due to niobium or niobium oxide [3,4].

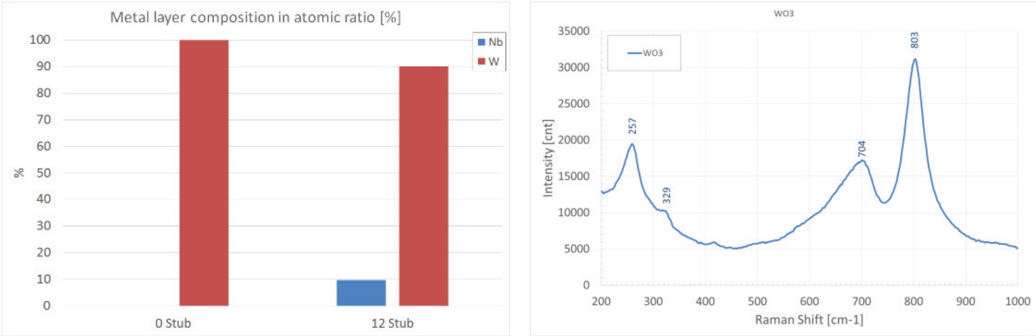

Fig. 2. (Left) EDX analysis on bulk and Nb-doped substrates. (Right) Raman spectrum of WO_3 nanowires

Samples were tested at different operating temperature toward a fixed concentration of 500ppm of hydrogen, as reported in Fig. 3. The addition of niobium does not influence the optimal operating temperature, resulted in 200°C. However, at this temperature the addition of niobium in the tungsten oxide nanowires increase the hydrogen sensing performance of about an order of magnitude. Only at 400°C Nb-added samples perform worse than bulk WO_3, but the overall response is far below the one at 200°C.

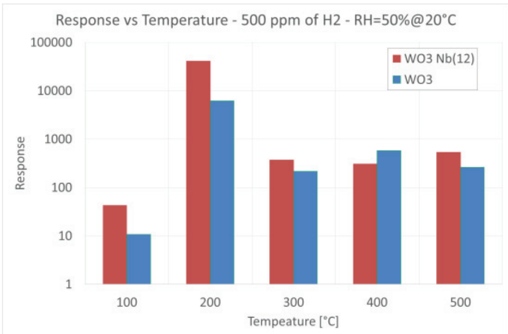

Fig. 3. Response vs Temperature towards 500ppm of hydrogen, at RH=50%@20°C.

Fig. 4 reports calibration curves and the response of both bulk and Nb-added WO_3 devices, at various hydrogen concentrations. From the picture is clearly visible that the adding of niobium to the structure increases the response toward hydrogen at medium and high concentrations. On the contrary, bulk WO_3 nanowires perform better at lower concentrations, less than 100ppm. Depending on the applications and end-user could choose between these two families of sensing device for the detection of hydrogen at ppm range.

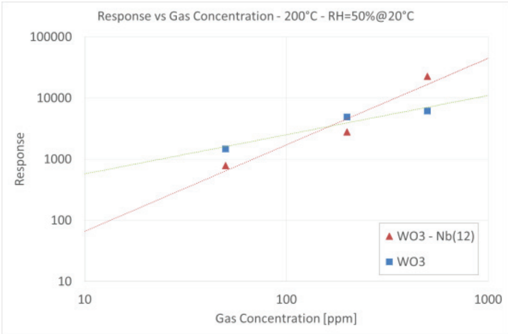

Fig. 4. Response vs Gas Concentration at 200°C, with RH=50%@20°C.

4. Conclusions

In this work, a comparison between the hydrogen sensing performance of both bulk and Nb-added tungsten oxide nanowires was performed. Nanowires were synthetized by a simple thermal oxidation technique in vacuum, and functional devices were fabricated. These gas sensors have an optimal working temperature of 200°C in the detection of hydrogen, and they are able to detect the target chemical compound at a ppm scale, and even less. In particular, bulk WO3 works better at concentrations lower than 100ppm, while the addition of niobium to the binary oxide enhance the sensing performance at concentration higher than 100ppm. Depending on required application, both material could be used in the detection of hydrogen.

Acknowledgements

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References

[1] T. Hübert, L. Boon-Brett, G. Black, U. Banach, Hydrogen sensors - a review, Sens. Actuators B 157 (2011) 329 – 352.
[2] Meng, D., Shaalan, N.M., Yamazaki, T. and Kikuta, T., Sens. Actuator B-Chem. 2012, 169, 113
[3] A. Rougier, F. Portemer, A. Quede and M. El Marssi, Appl Surf Sci, 1999, 153, 1-9.
[4] B. M. Weckhuysen, J. M. Jehng and I. E. Wachs, Journal of Physical Chemistry B, 2000, 104, 7382-7387.