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Gas-sensing properties of thermally-oxidized metal oxide nanowires

Dario Zappa[a]*, Elisabetta Comini[a], Giorgio Sberveglieri[a]

[a]*Sensor Laboratory, University of Brescia & CNR-IDASC, Via Valotti 9, 25133 Brescia, Italy*

Abstract

In this study metal oxide nanowires were grown by thermal oxidation of metallic thin layer deposited by sputtering on alumina and silicon substrates. Both n-type (ZnO) and p-type (CuO) nanowires were grown. Mat-based conductometric chemical sensing devices were successfully prepared, and their sensing response was evaluated towards different chemical species, in order to highlight the electrical properties of the materials. Calibration curves for the detection of some target gases were estimated.

Keywords: Metal oxides; Chemical sensing; Nanowires;

1. Introduction

Nanostructured materials are subject of an intensive scientific research because of their interesting properties and potential technological applications. Among the most promising nanostructures, metal oxide nanowires (NWs), nanobelts and nanorods deserve a special mention. Due to the high surface area/volume ratio and high crystallinity [1], nanostructured materials, in particular metal oxide NWs, are promising in the field of gas sensing [2] [3] [4] [5], for third generation solar cells [6] [7] and as field emitters sources [8] [9]. While the research focused mainly on n-type material (i.e. ZnO), little efforts have been made to investigate p-type material (i.e. CuO). In this study thermal oxidation technique was used to prepare ZnO and CuO nanowires directly from metal layers deposited on final device substrates. Mat-based device were successfully fabricated, and the conductometric response towards some chemical species were evaluated.

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2. Experimental

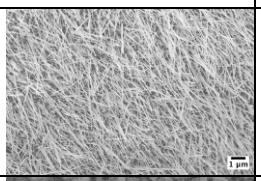
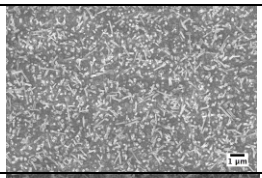
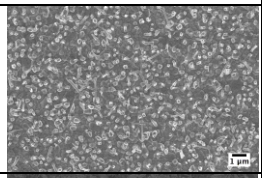
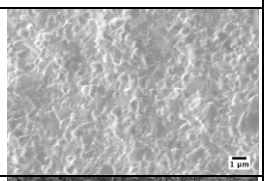
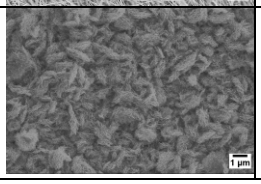
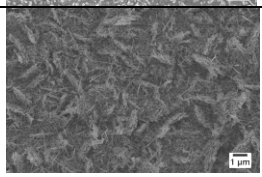
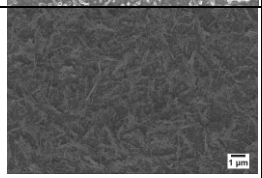
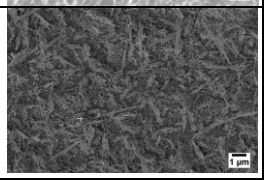
Thermal oxidation has a number of advantages compared to other growth techniques: it's scalable for mass-production and has a very high yield, with almost no cross-contamination between samples; it's a cheap method, working at atmospheric pressure; it's easy to pattern the growth area for example with shadow masking technique. The main disadvantage is the time required for a complete oxidation, in terms of hours. The growth process consisted into three phases: 1) substrate cleaning, performed in acetone with an ultrasonic cleaner; 2) metal deposition on the substrate, for example by magnetron sputtering or thermal evaporation; 3) thermal oxidation in a tubular furnace, introducing a mixed atmosphere of oxygen and argon.

RF magnetron sputtering was used to deposit thin films of metallic zinc and copper on various substrates, like alumina and silicon. A 50W argon plasma at room temperature was used to deposit both material, with a pressure inside the chamber of $5.3x10^{-3}$ mbar. Layer thickness was measured with a profiler resulting in 2µm for CuO and 4.5µm for ZnO.

Samples were then placed in a Carbolite tubular furnace for oxidation, operated by a PC home-made NI LabVIEW Virtual Instrument (VI). The morphology of NWs has been controlled changing the oxidation parameters, such as the oxidizing temperature and the oxygen/argon ratio in the introduced atmosphere. In particular, furnace's temperature strongly influenced the obtained morphology, especially in CuO (Table 1).

To investigate the morphology of metal oxide nanostructures, a field-emission scanning electron microscope SEM LEO 1525 was used, operated in a 3-5kV voltage range. Samples were attached with carbon glue to a metallic stub, to reduce the charging effect due to the electron beam. The resulting morphology of CuO and ZnO NWs, respect to the oxidation temperature, is reported in Table 1.

Table 1: Influence of the oxidation temperature on the morphology of the resulting nanostructures, for both ZnO and CuO. CuO NWs grew at temperature from 300°C (disordered mats) to 400°C (almost vertically aligned), while ZnO NWs grew from 400°C to 600°C with almost the same morphology.

	300 °C	400 °C	500 °C	600 °C
CuO				
ZnO				

Conductometric mat-based devices were prepared depositing interdigited platinum contacts on the front side of samples by DC magnetron sputtering, while a platinum heater was deposited with the same technique, to thermally activate metal oxide interaction with the surrounding atmosphere. The substrate was bonded on 4-pins TO package by electrosoldering gold wires from TO pins to device pads.

A home-made test chamber was used to evaluate the conductometric response of the prepared devices in presence of various target gases. This equipment consists in a climatic chamber (set at 20°C) able to measure up to ten sensors at the same time. MKS mass flow controls the gas flows inside the chamber,

including the aqueous vapour needed to select the humidity level (set at 50% for all measurements). A power supply, one for each sensor, controls the temperature of the devices, from room temperature up to 600°C. A batch of identical samples was prepared, in order to evaluate the stability and reproducibility of the devices. First, a screening in temperature was performed, to maximize sensor response. Conductometric measure shows the different behavior of n-type and p-type materials (Fig. 1), and the higher response of ZnO NWs compared to CuO NWs towards ethanol, as reported in literature [10] [11]. Then, a calibration curve towards ethanol was estimated for both n-type and p-type materials (Fig. 2). High reproducibility of the response was achieved, with a standard deviation less than 15% inside the batch.

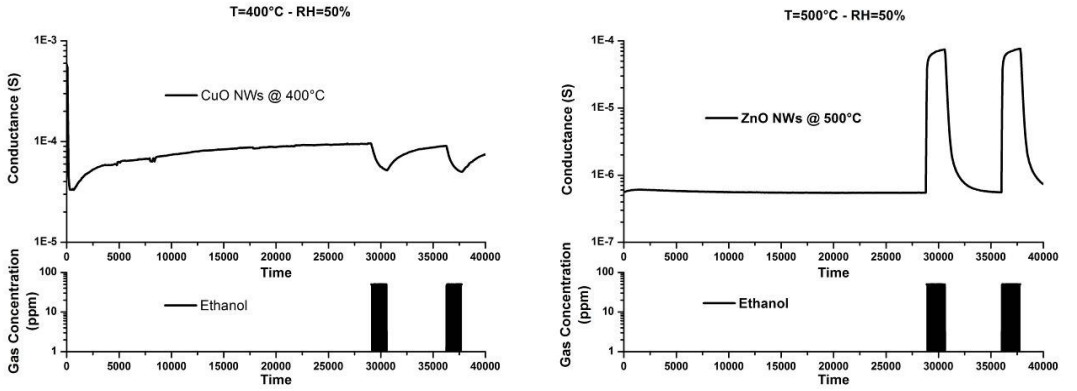


Fig 1: Dynamic response of CuO (at 400°C) and ZnO (at 500°C) NWs towards 50ppm of ethanol. The different behavior of n-type and p-type materials it is shown. Relative humidity was set at 50% for both measurements.

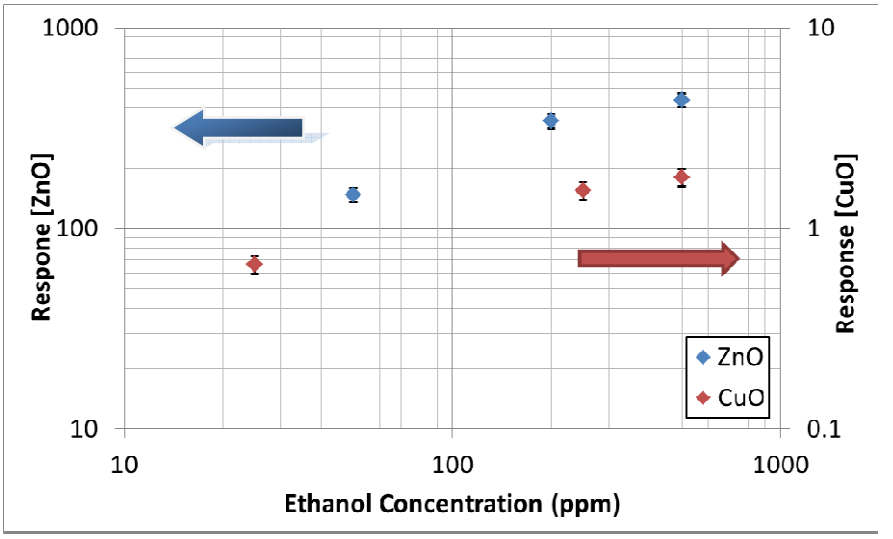


Fig. 2: Response of CuO NWs (at 400°C) and ZnO NWs (at 500°C) NWs towards different concentrations of ethanol. ZnO NWs shows a better response than CuO NWs. Relative humidity was set at 50% for both measurements.

3. Conclusions

Some sensing devices, starting from thermally oxidized CuO and ZnO NWs, were fabricated. The conductometric response towards some chemical species was measured. While reproducibility of the devices was very high for both ZnO and CuO, ZnO NWs showed higher response towards ethanol compared to CuO NWs, as reported in literature. The n-type and p-type behavior of the materials was undirected confirmed by the conductance variations in presence of target gas.

Acknowledgements

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