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Zinc oxide nanowires deposited on polymeric hotplates for low-power gas sensors

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Abstract

Zinc oxides (ZnO) nanowires were successfully deposited on plastic low-power micro-hotplates using the thermal oxidation technique. Metallic zinc layer was deposited on the sensing transducer by RF magnetron sputtering and then oxidized in a controlled atmosphere in order to obtain ZnO nanostructures. Morphological investigations confirmed the nanometric dimensions of the fabricated nanostructures. The n-type behavior of the nanostructured material was evaluated towards different chemical species to highlight the electrical properties of the materials. Calibration curves for the detection of several chemical species were defined.

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1. Introduction

Micro-hotplates are the key elements to reduce the power consumption of metal-oxide type chemical sensors, enabling their use in a wide range of applications where energy is the main constraint. Thanks to the micro-size dimensions it is possible to achieve a power consumption reduction of almost one order of magnitude. Recently, low-power micro-hotplates for metal-oxide gas sensors made on polyimide substrates were reported [1]. Low-power operation was achieved with simplified processing compared to Si technology, allowing potential production at very low-cost using large scale fabrication techniques (e.g. R2R). However, besides thin and thick films metal-oxides, there is an interest for using better performing

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materials requiring lower processing and operating temperatures. Nanowires (NW) offer better surface-to-volume ratio compared to other nanostructures, and thus they show better chemical sensing performances compared to bulk materials [2][3].

Zinc Oxide is by far the most studied metal oxide material. It's usually grown as an *n*-type semiconductor, due to oxygen vacancies, Zn interstitial or defect complex [4]. Thermal oxidation was used to grow ZnO nanowires directly on the polyimide substrates, starting from a metallic zinc layer. This technique is scalable for mass-production, and compatible with the use of plastic micro-hotplates, thanks to the low growth temperature. Substrates were then mounted on TO packages and their sensing performances toward some chemical species were evaluated.

2. Experimental

2.1. Device fabrication

A metallic zinc layer (800 nm) was deposited onto polymer hotplates by RF magnetron sputtering at room temperature, using a 50 W Argon plasma (pressure 5.3×10^{-3} mbar), using a shadow mask to pattern the deposition area. Samples were then placed in a LabView-controlled tubular furnace. They were oxidized in a mixed atmosphere (80% O₂ – 20% Ar) for 12 h with a constant flow of 300 sccm. The oxidation temperature inside the furnace was set to 300°C to avoid damaging the polymeric hotplates. During the annealing treatment, the metallic Zn completely oxidized, producing ZnO NWs.

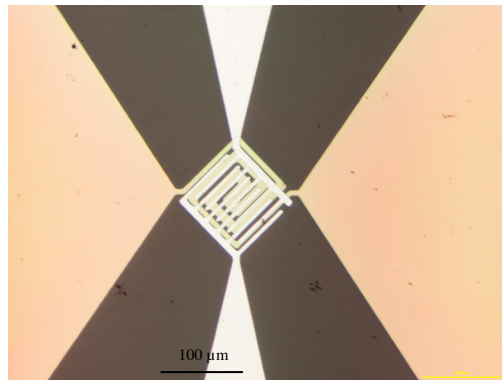


Fig. 1: Picture of the polymeric micro-hotplate. The area of the interdigitated electrodes and of the heater are $100 \times 100 \mu\text{m}^2$.

2.2. Morphological characterization

To investigate the morphology of metal-oxide nanostructures, a field-emission scanning electron microscope FE-SEM LEO 1525 was used with an acceleration voltage between 3 and 5 kV. The samples were attached to microscope stubs using carbon glue to avoid charging effect.

2.3. Functional characterization

For the evaluation of the conductometric performances of the sensor towards chemical species, a home-made test chamber was used. Up to four devices could be simultaneously measured, and the applied

voltage to the device sensing layer was 1 V. The film conductance was measured by a Keithley 486 picoammeter. Relative humidity was controlled and set to 50%. A constant flow of synthetic air of 0.3 l/min was used as carrier gas, into which the desired concentration of test gases was mixed. The samples were held at the desired power level for 8 h for stabilization. After a target gas exposure of 30 min, recovery occurred in synthetic air for 90 min.

3. Results and Conclusions

The obtained morphology after the thermal oxidation in the tubular furnace is reported in Fig. 2, a dense mat of nanowires was produced over the oxide thin film.

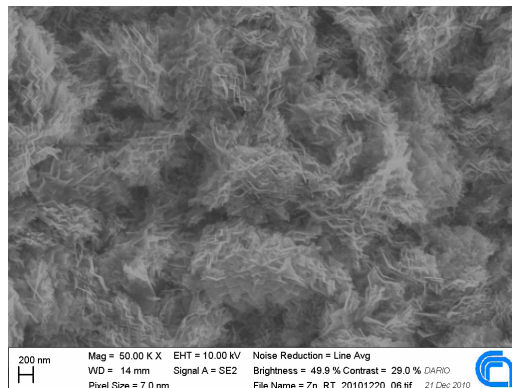


Fig. 2: ZnO nanostructures prepared at 300°C in an 80% O₂ – 20% Ar atmosphere.

The n-type behavior of the metal-oxide structures was confirmed (Fig. 3). The reaction between ZnO and an oxidizing gas like NO₂ led to a decrease of conductance. Different levels of electric power were applied to the micro-heaters to study the effect of the temperature on the sensor's response. Then, a calibration curve towards some chemical species was estimated for some of the power levels applied (Fig. 4). High reproducibility of the response was achieved, together with a very good response to nitrogen dioxide.

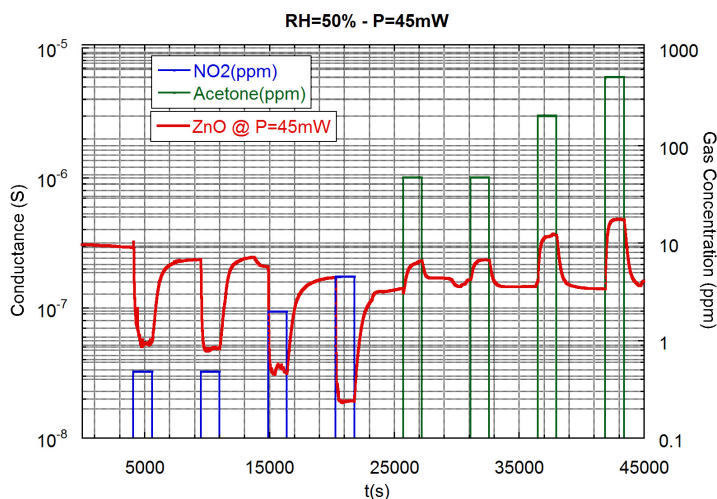


Fig. 3: Dynamic response of ZnO micro hotplate, with an applied power of 45mW. Relative humidity was set at 50%.

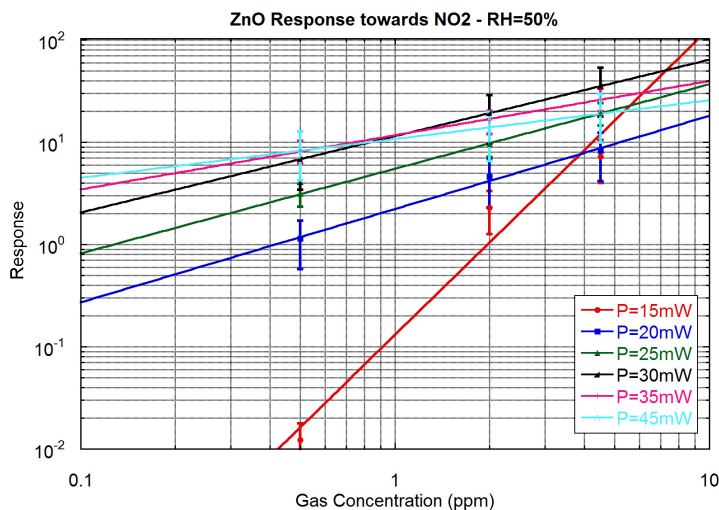


Fig. 4: ZnO micro hotplate response towards NO₂ with various levels of power applied. Response is defined as $(G_{\text{air}} - G_{\text{gas}}) / G_{\text{gas}}$. Relative humidity was set to 50%.

In summary, we demonstrated the compatibility of processing nanowires with polyimide micro-hotplates, resulting in high performances low-power gas sensors. The deposition technique used is also compatible with other materials, such as CuO for example. Thus it could be used to produce arrays of nanowire-based chemical sensors for a wide range of applications.

Acknowledgements

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