GROWTH OF ZNO TETRAPODS FOR GAS SENSOR APPLICATION

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Abstract: Zinc Oxide (ZnO) nanostructures have been obtained by vapour phase growth. Tetrapods have been grown on a large scale, in a reproducible way and separated from the other possible ZnO nano-morphologies, by the optimization of growth parameters. The deposition of these nanostructures on an alumina substrate with contacts and heater, allowed us to realize a low-cost oriented gas sensor. The obtained ZnO tetrapods-based gas sensor prototypes have been tested with different gases.

Keywords: zinc oxide, tetrapods, gas sensor

INTRODUCTION

Among metal oxides, tin oxide (SnO_2) is surely the most used material in gas sensor field. But other oxides are often used to enhance sensitivity and/or selectivity to some specific gas or in view of application in multi-sensors arrays.
Because of their peculiar physical and chemical properties, quasi-1D nanostructures of metal oxides (nanowires, nanobelts, nanotubes, nanorods, nanosprings, etc.) called researchers' attention to the possible application of these materials in the realization of gas sensors [1].
Zinc Oxide (ZnO) nanostructures can be obtained by vapor phase growth in a large variety of morphologies (widely reported in literature – e.g. see [2-4]) and they are today employed in many different applications, such as photovoltaics, optoelectronics, photocatalysis, etc.
Some efforts have been also done to test the gas sensing properties of ZnO nanostructures. ZnO nanowires have been mainly studied, because of their linear and more promising morphology, while only a smaller attention was devoted to ZnO tetrapods. Nevertheless, among the observed morphologies, tetrapods are particularly interesting because of the possibility to get very large yields in the synthesis process.
A deep study has been performed by this group to optimize the vapor phase synthesis process in order to get reproducible and selected growth of tetrapods only. The obtained nanostructures have been used to realize some low-cost tetrapods-based sensor prototypes to test their response to different gases.

SYNTHESIS

It is well known that ZnO can be obtained in many different nanostructures with unique morphologies. However, it is quite common to get some of them mixed together in the same growth process, since even very small fluctuation in the local growth parameters (Zn vapor and O_2 partial pressures, Zn/O ratio, liquid Zn condensation/evaporation rate, nucleation conditions, etc.) may lead to the formation of a different nanostructure.
Single selected ZnO nanostructures can be obtained on a large scale only through an accurate study of the synthesis process dynamics and a refinement of the growth parameters. For example, in the proper conditions a Zn metallic layer can be used on the substrates as a catalyst for the growth of long ZnO nanowires [5].
Tetrapods, instead, generally nucleate and grow in the vapor stream and they can be collected at the end of the reactor's tube in form of a large and dense network of nanostructures.
A large amount of ZnO tetrapods (Fig. 1) has been obtained in a tubular furnace by heating the source material (metallic Zn, 99,999% pure) at 600°C and by flowing, subsequently, an Ar/O_2 mixture (20:1 ratio – 100sccm flow) in the reactor.
No catalyst or precursor has been used in order to reduce as much as possible unwanted contaminations.

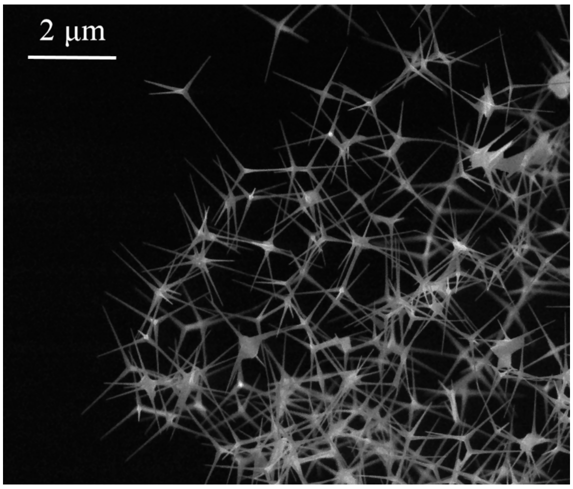

Figure 1. SEM image of some of the grown ZnO tetrapods

The obtained material morphology and structure have been studied by mean of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD) measurements.

The length of tetrapods “legs” usually ranges from 1_m to 20_m and their cross section from 10nm up to 1_m. Two different types of tetrapods have been observed: a) with constant leg thickness and b) with leg thickness that decreases from the tetrapod core to the leg tip. The latter is generally the dominant type. However, in both cases the tetrapod legs grow along the *c* axis of the hexagonal wurtzite-like crystal structure.

Photoluminescence (PL) emission has been also carried out by exciting the samples with a He-Cd laser emitting at 325 nm. The obtained spectra showed a very intense emission even at room temperature (Fig. 2). The main emission has been found at about 382 nm (Eg= 3.38eV_370nm at 300K). The PL spectra obtained on these samples are much simpler than those often reported in the literature for ZnO nanostructures. In particular, very weak emission was detected in either green or orange regions, indicating a good crystalline quality.

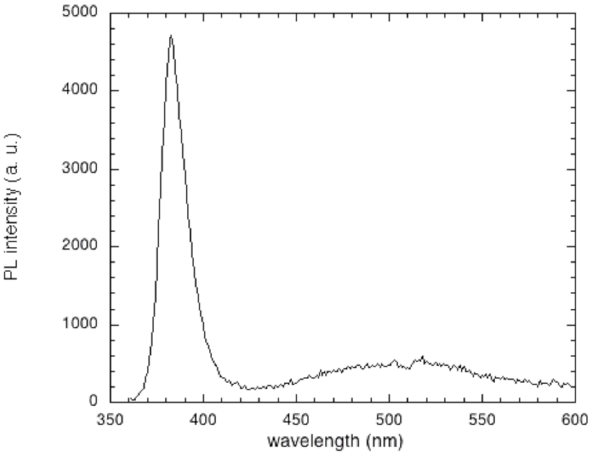

Figure 2. Room temperature PL spectrum of ZnO tetrapods

GAS SENSOR

As told before, one of the most interesting aspects of ZnO tetrapods growth is the large yield which can be reached in the synthesis process. This is a fundamental and propelling characteristic for the realization of a low-cost device.

An easy procedure for the realization of a ZnO tetrapods based gas sensor has been defined and the properties of the obtained device have been tested.

The target of a low-cost device was the driving idea since the beginning and thus a simple geometry has been designed for Au contacts and the Pt heater, with parallel sensor and heating element on the same side of an alumina substrate (Fig. 3).

Figure 3. Schematic draw of the sensor contacts and heater geometry.

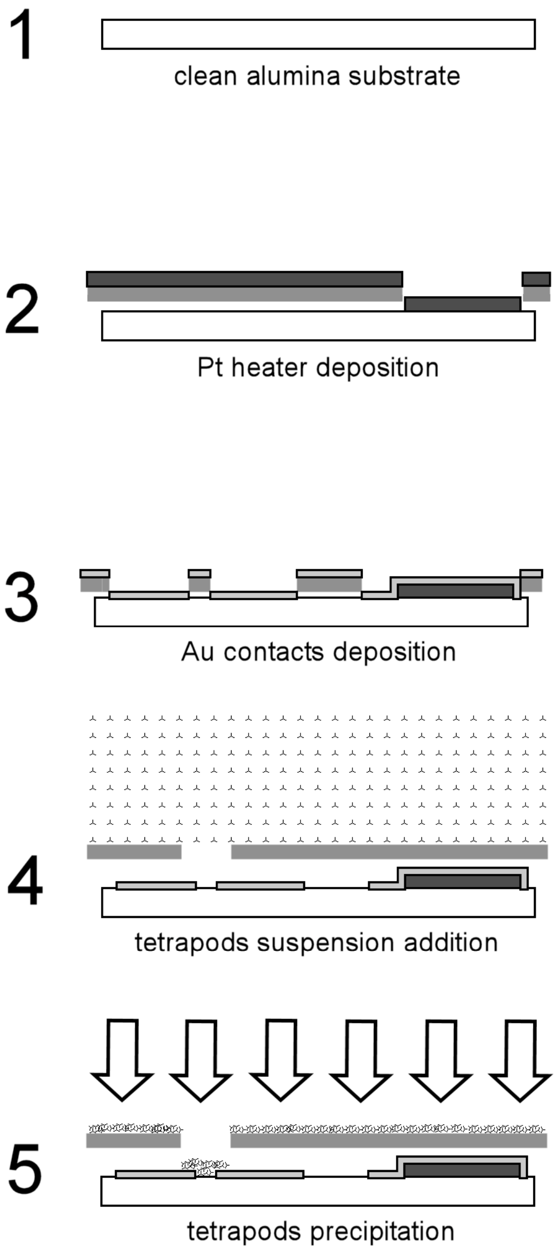

Figure 4. Simplified outline of the different steps of the sensor preparation procedure

Obviously this device geometry implies a temperature gradient between the heater and the sensing material but the sensor temperature can be exactly defined with thermo- and fluid-dynamics simulations and experimental calibrations. On the other hand this design allows to strongly simplify the production process and the bonding procedure.
In this configuration the thermal gradient on the alumina substrate is nearly linear along the direction which is perpendicular to the heater, while it is negligible along the parallel direction.
ZnO tetrapods have been deposited over the two proper contacts by mean of a simple mechanical mask. An optimized alcoholic suspension of these nanostructures is prepared and then they are precipitated through the mask in the proper zone of the substrate (Fig. 4).
Some sensor prototypes have been prepared with this procedure. The sensors have then been treated to remove the residuals of the alcoholic liquid and finally bonded to perform conductometric gas response tests (Fig. 5).

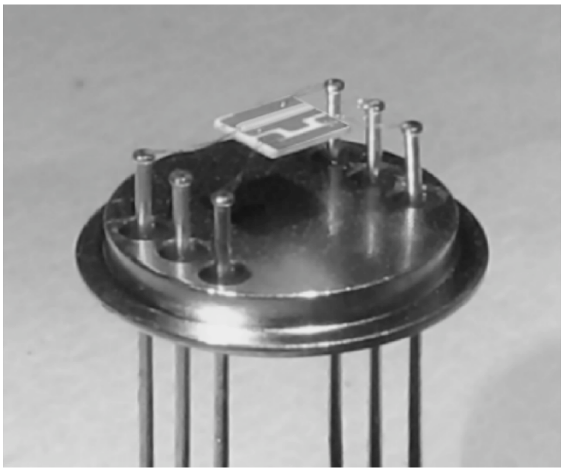

Figure 5. ZnO tetrapods-based gas sensor

A simple check has revealed that the deposition film of ZnO tetrapods is mechanically stable even when a 1 m/s gas flow is directed on the sensor.
The sensor has been tested with some of the commonest gas, as ethanol, CO, NO_2 and H_2S.
In particular, interesting results have been obtained with hydrogen sulphide (H_2S). Values close to the H_2S TLV (Threshold Limit Value), i.e. 10 ppm ≈ $15 mg/m^3$, have been tested and a very high response has been obtained (Fig. 6-7).
Defining the Response % value as:

$$R = (G_{gas} - G_{air}) / G_{air} \times 100$$

where G_{air} is the sensor conductivity in dry air and G_{gas} the conductivity in presence of the gas, maximum values of 9250% and 2200% have been obtained at 300°C for 5ppm of H_2S and 1ppm of H_2S respectively. Thus, H_2S sensitivity is very high in this "useful" safety-monitoring concentration range.

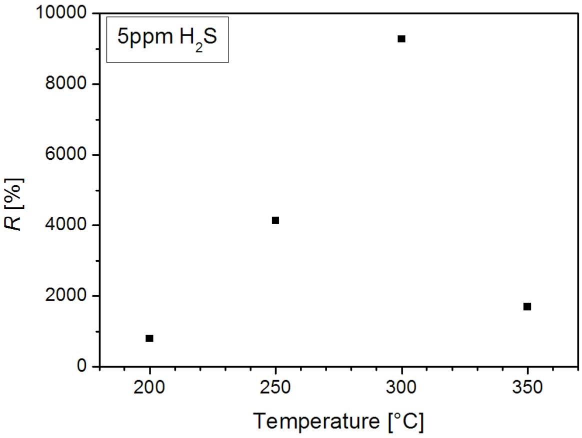

Figure 6. Response to 5 ppm of H_2S as a function of temperature, measured in dry air condition (0% relative humidity) with a 500ml/min flow.

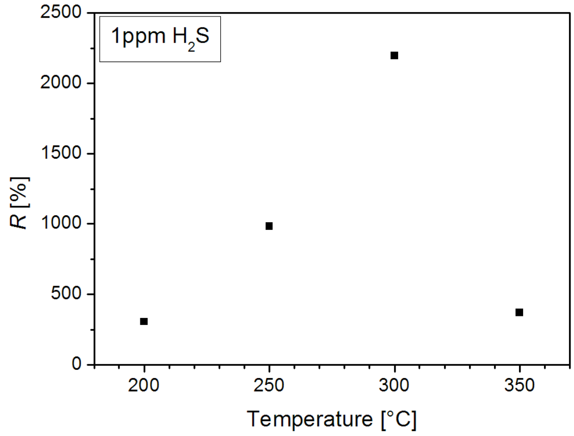

Figure 7. Response to 1 ppm of H_2S as a function of temperature, measured in dry air condition (0% relative humidity) with a 500ml/min flow.

Moreover, the current value in the sensor generally ranges between 1_A and 1mA when 5V are applied. These current values can be considered "compatible" with a low-cost electronic interface.

CONCLUSIONS

A large yield synthesis process for the growth of ZnO tetrapods has been defined. In view of the realization of a low-cost tetrapods-based gas sensor device, some prototypes have been realized and tested. Promising results have been obtained. Especially, high response and sensitivity have been found in the detection of H_2S.

REFERENCES

1. X. J. Huang, Y. K. Choi, *Sensors and Actuators B,* 122 (2007), 659
2. Z. L. Wang, *Materials Today,* 7 (2004), 26

3. Z. L. Wang, *J. Phys.: Condens. Matter,* 16 (2004) R829
4. Z. L. Wang, *Materials Today,* 10 (2007), 40
5. M. Zha, D. Calestani, A. Zappettini, R. Mosca, M. Mazzera, L. Lazzarini, L. Zanotti, Nanotechnology, 19 (2008), 325603