High-sensitivity indoor-air-quality sensor through localized growth of ZnO nanostructures

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Abstract

The aim of this work is to develop an easy-to-manufacture and highly-sensitive conductometric microsensor for indoor air quality (IAQ) monitoring. The sensing material is nanostructured ZnO on Pt electrodes. A Pt heater surrounds the ZnO, so the whole sensor is fabricated on one side of a 2,5x2,5 mm² alumina substrate. ZnO nanostructures are grown in-situ over the electrodes, using the Vapour-Solid (VS) approach. The samples have been tested under different concentrations of benzene, formaldehyde and nitrogen dioxide, showing significant response to low concentrations of the three gases.

1. Introduction

Metal oxide materials have been widely investigated in the last years due to their usability in different applications such as gas sensors, optoelectronic sensors, resonators and light emitting devices. These materials present several advantages as scalability, flexibility associated to their production, low cost and simplicity of use.

Conductometric gas sensors based in MOXs have been extensively researched and even reached the consumer market. Materials such as SnO₂, ZnO, TiO₂, WO₃ and NiO have been popularly used as sensing material for different purposes such as environmental monitoring and chemical process control [1].

Several techniques have been described in the literature for MOX nanostructure growth, including vapor-phase transport processes, chemical vapor deposition, arc-discharge, laser ablation, and solution and template-based methods [2]. Nanostructure growth techniques are widely investigated in this field because MOX in this form are considered promising materials to be used as sensing layers due to their high surface-volume ratio [3]. Furthermore,
a fast response and recovery are expected due to their porous morphology improving gas diffusion, and also to possible changes in the conduction mechanism [4].

But it is also important to keep a simple fabrication process while reaching high repeatability in the process. For this reason, the development of routes to grow localized nanostructures is highly interesting, because they do not add any extra step in the fabrication process. This work shows the fabrication, characterization and test of a conductometric microsensor with ZnO nanowires as sensing material [5], directly grown on Pt electrodes (obtained by sputtering) through the VS technique.

2. Experimental details

2.1. Nanostructure growth

The nanostructure growth process is based on the vapour-solid method. As shown in Fig. 1, the first step consists on depositing a zinc thin film over the alumina substrate by RF sputtering. The sputtering process is carried out in argon atmosphere at a pressure of $5 \times 10^{-3}$ mbar in the chamber and 150W of applied power. Once the thin film is deposited, the samples are annealed in a tube furnace (PEO 601 from ATV) in ambient pressure. As the temperature is increased in nitrogen ambient, Zn film starts to melt and small particles are formed. Then, a low flow of oxygen is entered in the furnace, so Zn particles are oxidized forming ZnO nanoparticles. A continuous diffusion of Zn atoms and a continuous oxidation produces the growth of nanostructures.

The influence of different parameters of the annealing process in the nanostructure growth has been studied. The annealing temperature has been changed in the range of 500-900°C, the oxygen flow in the range of 55-250 sccm, and three different layer thicknesses of Zn layers have been studied. Ar has also been tried as inert gas during the heating and cooling process.

2.2. Sensor device fabrication

The fabrication process of the whole sensor is summarized in the Fig. 2. First, Pt microelectrodes are grown on the alumina substrate by DC sputtering using the conventional lift-off process (steps 1 to 3). The platinum thin film microelectrodes are 300 μm length, 20 μm width and the separation among fingers is 20 μm. In the next step, Zn is deposited by RF sputtering over the electrodes (steps 4 and 5) with a 0.5x0.5 mm area. Finally, the optimized VS process explained in the previous section is carried out in nitrogen and oxygen controlled flow at high temperature. Depending on the annealing parameters, either 1D nanostructures or thin films with nanodimensional grains can be obtained (step 6). Once the chips are fabricated, they are mounted on TO5 packages for electrical characterization.

Fig. 1. VS process for nanostructure growth.

Fig. 2. Sensor fabrication process.
3. Material characterization

The structural properties of the nanostructures were analyzed using a Philips XPERT MRD diffractometer (Cu K\(\alpha\) \(\lambda\)=1.54059 'A). In the XRD pattern of the ZnO nanostructures grown by VS process, the alumina and zincite XRD patterns [6] were compared concluding that the peaks that do not fit the zincite pattern are caused by the alumina substrate and not by non-oxidized zinc particles or other impurities. It also shows that the as-deposited zinc film was completely oxidized.

The nanostructures were also analyzed using the Scanning Electron Microscope (SEM) and an Atomic Force Microscope (AFM). Fig. 3 shows a SEM micrograph where ZnO nanostructures with an average grain size of 60 nm and a rms roughness of 230 nm calculated from AFM images can be observed.

![SEM micrograph of the nanostructures.](image)

Fig. 3. Microsensor design and SEM micrograph of the nanostructures.

4. Sensing properties

To investigate the conductometric response of the sensor under different gases, the samples were placed inside of a 44 ml chamber and resistance changes in presence of different concentrations of gases were measured using a Keithley 2000 Multimeter. Using the mentioned set-up the answer to three different gases was measured: benzene, formaldehyde and nitrogen dioxide. The total flow inside the chamber was 400 sccm and different concentrations of target gases were obtained mixing them with synthetic air.

Formula (1) defines the sensor response as the ratio between the resistance baseline in air and the resistance measured in presence of the target gas (oxidizing), where \(R_{\text{gas}}\) is the sensor resistance in presence of gas and \(R_{\text{air}}\) is the sensor resistance in air.

\[
SR[\%] = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} = \frac{R_{\text{gas}}}{R_{\text{air}}}
\]

(1)

There are several organisms that determine different hazard levels as a function of the concentration and time a human is exposed to a certain gas. Table 1 shows the short-term exposure levels (STEL), Immediately Dangerous to Life or Health levels (IDLH), Permissible Exposure Levels (PEL) and Action levels for benzene, formaldehyde and nitrogen dioxide. Taking the regulations into account, the range between 20 ppm and 50 ppb was chosen for the experiments.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>IDLH</th>
<th>STEL</th>
<th>PEL</th>
<th>Action level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>500 ppm</td>
<td>2.5 ppm</td>
<td>1 ppm</td>
<td>500 ppb</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>20 ppm</td>
<td>0.75 ppm</td>
<td>0.75 ppm</td>
<td>500 ppb</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>20 ppm</td>
<td>5 ppm</td>
<td>5 ppm</td>
<td>300 ppb</td>
</tr>
</tbody>
</table>
The sensor responses to the three target gases are shown in Fig. 3a, while Fig. 3b shows the sensitivity curves of the ZnO sensor working at 265°C. As can be observed, the sensor shows higher response to nitrogen dioxide but it is also able to detect formaldehyde and benzene, so as most MOX sensors, it exhibits a lack of selectivity.

Fig. 3. (a) Sensor response to different concentrations of benzene, formaldehyde and nitrogen dioxide. (b) Sensitivity curves for target gases.

Analyzing the data obtained from the sensor response, detection limits, sensitivities and response times of the sensor at different concentrations for each target gas were calculated and are summarized in Table 2. The lowest detection limits achieved for these gases are 500 ppb for the benzene and 50 ppb for the formaldehyde and nitrogen dioxide, at least as low as the OSHA action levels require. Response times are also short enough to use this sensor in IAQ measurements.

Table 2. Summary of obtained results.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Limit of detection</th>
<th>Sensitivity</th>
<th>Response time (PEL)</th>
<th>Response time (10 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>100 ppb</td>
<td>1.83 %/ppm</td>
<td>8 min</td>
<td>2 min</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>50 ppb</td>
<td>2.31 %/ppm</td>
<td>4 min</td>
<td>1 min</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>50 ppb</td>
<td>12.6 %/ppm</td>
<td>2 min</td>
<td>3 min</td>
</tr>
</tbody>
</table>

5. Conclusions

The present study has shown the sensing properties of a ZnO nanostructured sensor under benzene, formaldehyde and nitrogen dioxide. After studying the influence of the oxygen flow, annealing temperature and zinc layer thickness in the material growth, 110sccm of oxygen, 550°C as annealing temperature and 1μm thickness values have been selected as optimum values for the sensor fabrication. By this simple fabrication process, nanowires were grown directly and precisely over the electrodes for electrical characterization. The sensor was tested at an operating temperature of 265°C and ppb concentrations of benzene, formaldehyde and nitrogen dioxide were measured. It is a promising sensor for IAQ monitoring, providing low detection limit and fast response times. The lack of selectivity observed in this sensor could be improved using it as a part of an array of MOX sensors based on different materials.

References