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ZnO-based gas microsensors sensitive to CO at room temperature by photoactivation

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Abstract

Gas microsensors based on ZnO structures grown *via* aerosol-assisted chemical vapor deposition are fabricated. The photoactivated and thermoactivated gas sensing properties of these systems toward CO are presented. Results demonstrate photoactivated responses at room temperature with improved characteristics, which include 35 % higher response and 7% faster response times, compared to the thermoactivated response of the sensors at 250 °C. This characteristic becomes significantly advantageous as it allows for the sensor to operate without integrated heaters minimizing the power consumption of the system.

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Keywords: ZnO, gas sensors, CO, room temperature, photoactivation

1. Introduction

ZnO is a highly versatile material with chemical, electrical and optical properties that make it an ideal material to be used in photoactivated gas sensing. However, despite this, there is few information in the literature related to the photoactivated gas sensing properties of this material. The literature related to the synthesis of ZnO, in contrast, describes the use of various wet- and vapor-phase routes for achieving ZnO structures. Thus, ZnO structures in the form of rods or wires have been synthesized previously *via* vapor-phase routes (typically using pre-grown catalyst

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seeds, i.e., *via* vapor-liquid-solid (VLS) mechanism and/or high temperatures from 900 to 1300 °C [1], which requires extra surface pre-treatment processing step and/or adds potential technological limitations for device fabrication). Recently, however, we have recognized that aerosol-assisted chemical vapor deposition (AACVD), a vapor-phase route, can lead to a structured growth of metal oxides at lower temperatures and without the need for catalyst seeds, i.e., *via* vapor solid (VS) mechanism.[2, 3] Therefore, here we report the fabrication of gas microsensors based on structured ZnO synthetized without the need of substrate pretreatment at 400 °C *via* AACVD and the photoactivated properties of these systems towards carbon monoxide.

2. Materials and Methods

The microsensors were fabricated by micro-electro-mechanical systems technology and consisted of a suspended membrane, containing resistive microheaters and interdigitated microelectrodes insulated by an interlevel silicon oxide layer. The ZnO structures were integrated directly on the top of the electrodes *via* AACVD, using the system described previously [4]. The area of deposition was controlled by using a shadow mask that confined the film deposition into the membrane area and protected the electrical contacts. Subsequently the chips were mounted and bounded on a TO-8 package.

The morphology of the films was examined using scanning electron microscopy (SEM – Tescan FE Mira II LMU) and the phase using X-ray Diffraction (XRD – Rigaku SmartLab 3 kW, Cu Kα radiation). Further analysis of the material was carried out using transmission electron microscopy (TEM – JEM 2100F operated at 200 kV using a Schottky cathode and equipped with EDX).

The microsensors were tested in a continuous flow (50 sccm) test chamber [4] provided of mass flow controllers and continuous illumination from a lamp with wavelength of 147 nm (CDL 1021-0X, Analytical Control Instruments). The sensors were exposed to CO during 60, 120, 240, 600, or 1200 s and subsequently the analyte was purged with air (3X,Praxair) until initial baseline resistance in air was recovered. The sensor response was defined as $R = R_{air}/R_{CO}$, where R_{air} and R_{CO} are the resistance in air and CO, respectively. The response time was defined as the time required for the sensor to reach 90% of the sensor response.

3. Results and discussion

SEM of the films displayed a morphology characterized by a high density of quasi-aligned hexagonal-shaped rods with diameters of ~380 nm (**Fig. 1a**). XRD revealed the presence of a hexagonal ZnO phase (P63mc space group, a = 3.2490 Å, b = 3.2490 Å, c = 5.2050 Å; ICCD card no. 5−0664), with a high intensity peak at 34.34° 2θ (d=2.60 Å) that indicate a strong preferred orientation in the [001] direction. Further analysis on the properties of the ZnO particles was achieved by EDX and TEM. EDX of the particles confirmed the presence of Zn and revealed relatively low chlorine contamination (found for Cl:Zn 0.05 *at*.%), whereas TEM (**Fig. 1b**) displayed marked planar spacing (0.26 nm), consistent with the internal lattice of the (002) plane (d = 0.26025 nm) of the phase identified by XRD, demonstrating that the ZnO structures grown *via* AACVD are single-crystalline with the growth in the [001] direction.

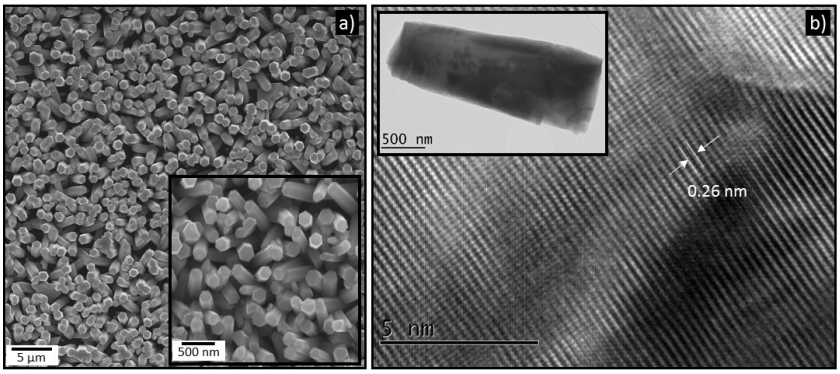

Fig. 1. Low and high magnification SEM (a) and TEM (b) images of the gas sensitive ZnO structures.

Thermoactivated results showed sensor responses for temperatures exceeding 125 °C, with the highest values registered at 305°C, whereas photoactivated results demonstrated sensor responses at room temperature with faster response to CO and greater resistance changes than those observed in the thermoactivated test at 250 °C (**Fig. 2** and **Fig. 3**), which is consistent with that observed for other metal oxide systems, when comparing their performance in thermoactivated and photoactivated mode.[5] The photoactivated tests also displayed better stability of the baseline resistance (**Fig. 3a**) at room temperature compared to that at 250 °C, although long recovery times were needed to re-establish the initial baseline resistance after CO exposure (e.g., 2400 s for 300 s of CO exposure).

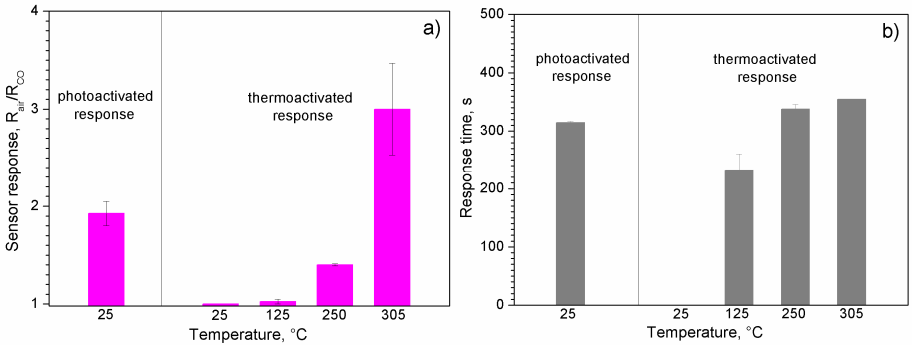

Fig. 2. Sensor response (a) and response time (b) to 100 ppm of CO in photoactivated or thermoactivated mode. The sensor response was defined as R_{air}/R_{CO} (where R_{air} is the sensor resistance in air and R_{CO} represents the sensor resistance after 600 s of CO exposure), whereas the response time was defined as the time required for the sensor to reach 90% of the sensor response.

The conductivity changes of ZnO at room temperature towards CO, when using photoactivation, are more likely connected with the generation of photoexcited electrons at the surface of the rods. These photoexcited electrons contribute to the formation of a higher density of preadsorbed ionic oxygen at the ZnO surface at room temperature and thus to a higher amount of active sites for the oxidation of CO, as compared to the non-photoactivated or non-thermoactivated process.

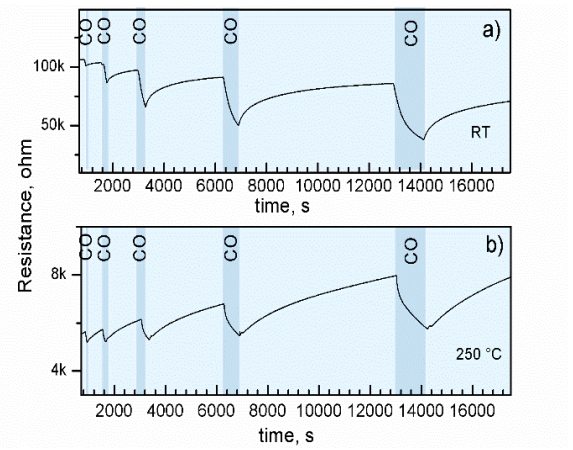

Fig. 3. Film resistance changes towards 100 ppm of CO at room temperature (photoactivated response) (a) and 250 °C (thermoactivated response) (b). Sensors were exposed to CO for different periods of time (60, 120, 300, 600 and 1200 s).

A comparison of these results with those reported in the literature for other chemical vapor deposited ZnO [6] suggests improved gas sensing properties for the ZnO structures grown *via* AACVD, as opposed to other morphologies (**Table 1**). This improvement, particularly when the sensor operates at room temperature, is technologically significant as it allows for the sensor to detect CO without the need of integrated heaters and minimizing the power consumption of the system.

Table 1. Relative sensor response to ppm concentration of CO [(R×100)/C] and selected sensing test conditions for different chemical vapor deposited ZnO morphologies summarized in the literature [1] (data based on the maximum response for the minimum concentration reported in each work).

ZnO morphology	Test conditions	Top	(R×100)/C %
*Rods	thermoactivated	305	3
*Rods	photoactivated	RT	1.90
Hierarchical structures	N/A	RT	0.72
Wires	N/A	N/A	0.75
Particles	thermoactivated	300	0.15
Film	thermoactivated	300	0.10

** results obtained in this work*

4. Conclusion

Gas microsensors based on ZnO structures were developed using AACVD, and the photoactivated and thermoactivated gas sensing properties of these systems toward CO were presented. Test of the gas sensitivity of these structures showed promising results, particularly for their sensing properties at room temperature by photoactivation. The photoactivated responses at room temperature revealed 35 % higher response and 7% faster response times, compared to the thermoactivated response of the sensors at 250 °C.

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