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Tuning of the Humidity-Interference in Gas Sensitive Columnar ZnO Structures †

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Abstract: Gas microsensors based on columnar zinc oxide structures (rods and needles) with different aspect ratios and wetting properties are developed via aerosol-assisted chemical vapor deposition. The correlation between their wetting properties and degree of humidity-interference in gas sensing is presented. Gas sensing tests of these systems to hydrogen demonstrate noticeable lower humidity-interference for the columnar zinc oxide structures in the form of needles provided of higher hydrophobicity, as opposed to those in the form of rods, suggesting that a tuning of the wetting properties in metal oxides could allow for the humidity-resilient detection of gaseous analytes.

Keywords: gas sensor; humidity; ZnO; AACVD

1. Introduction

Zinc oxide (ZnO) is a highly versatile material that is used in electronics, catalysis or chemical sensing, among others. The use of ZnO as gas sensitive material dates back to the 1960s, nevertheless the gas sensing properties of this material are still studied intensively due to common drawbacks, also present in other metal oxides, such as the lack of selectivity and the strong humidity-dependence.

ZnO adopts a stable hexagonal wurtzite structure with its morphological forms (e.g., rods, needles, plates, etc.) generally dominated by nonpolar or polar facets that provide a specific electronic structure at the surface. Thus, the morphological control of ZnO as well as other metal oxides has found to be particularly important in surface-dependent applications such as gas sensing, as it allows the tuning of the properties of gas sensitive materials [1]. The first stage toward the morphological control of structures includes the use of synthetic methods (e.g., bottom-up) capable of producing well-defined crystals, with uniform size, shape, and surface structure. Vapor-phase routes, such as aerosol assisted chemical vapor deposition (AACVD), are bottom-up approaches, and are industrially attractive as they provide the ability to generate structured films in continuous mode, with high purity and high throughput.

Previously, the micro and nano structuration of materials has also demonstrated to play a role in the wetting behavior of ZnO surfaces [2], but the correlation of this behavior with the gas sensing properties of metal oxides has been discussed rarely in the literature. Recently, however, we have noticed that the tuning of the aspect ratios in columnar ZnO structures formed via AACVD not only has an impact on the wetting properties of its surface, but also on the degree of humidity-interference during gas detection. Here we report the formation of columnar ZnO structures with rod- and needle-like morphology via a non-catalyzed vapor-solid mechanism method enabled using AACVD, and the correlation between their wetting properties and degree of humidity-interference in gas sensing.

2. Materials and Methods

Columnar ZnO structures in the form of rods or needles were grown on either Si or Si-based micromachined platforms using the AACVD method described previously [3]. 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). Water contact angle measurements were characterized using a contact angle measurement device (Phoenix 300) using a drop volume of 10 μL and Surfaceware8 software.

Micromachined sensors consisted of a suspended membrane containing, from bottom to top, a resistive platinum heater, an interlevel silicon oxide layer, interdigitated platinum electrodes, and columnar ZnO rods deposited directly via AACVD (Figure 1). These microsensors were tested in a continuous flow system [4] with dry air as reference gas, and were exposed to either humidity or hydrogen diluted in dry air for 600 s. After each analyte exposition, the microsensors were recovered in dry air for 1200 s. To have a proper control of the relative humidity (RH) inside the gas test chamber an evaluation kit (EK-H4, Sensirion AG) with a humidity sensor (SHT71, operating ranges from 0 to 100% RH, accuracy of ±3% RH) was also used. Sensor responses were defined as Ra/Rg where Ra and Rg are the resistance in dry air and the resistance after 600 s of analyte exposure, respectively.

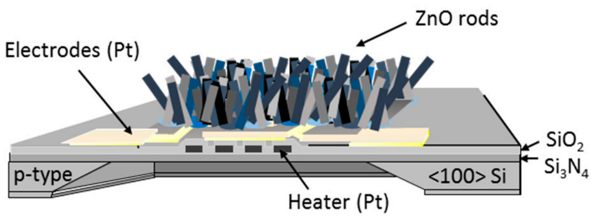

Figure 1. Schematic view of the micromachined sensor based on columnar ZnO structures.

3. Results and Discussion

SEM images of the ZnO films deposited via AACVD display a high density of quasi-aligned columnar structures with rod- (Figure 2a) or needle-like morphology (Figure 2b). Overall, these columnar structures are characterized by similar lengths with larger diameters for the structures in the form of rods compared to those in the form of needles, which correspond to aspect ratios of ~4 and ~11 for the rods and needles, respectively.

XRD of the rods and needles revealed the presence of hexagonal ZnO phase (P63mc space group, ICCD card no. 5–0664), with a high-intensity peak at 34.34° 2θ that indicate a strong preferred orientation in the [001] direction. Further analysis on the properties of the columnar structures was achieved by EDX and HRTEM. EDX analysis of these particles confirmed the presence of Zn with relatively low chlorine contamination (found for Cl:Zn 0.05 at. %), and HRTEM demonstrate the growth of structures in the [001] direction, evidenced by marked planar spacing of 0.26 nm, consistent with the internal lattice of the (002) plane of the phase identified by XRD. Moreover, the water droplets on the surface coated with rods or needles at room temperature displayed lower contact angle (120°) on the rods (Figure 2c), as opposed to the needles (134°) (Figure 2d).

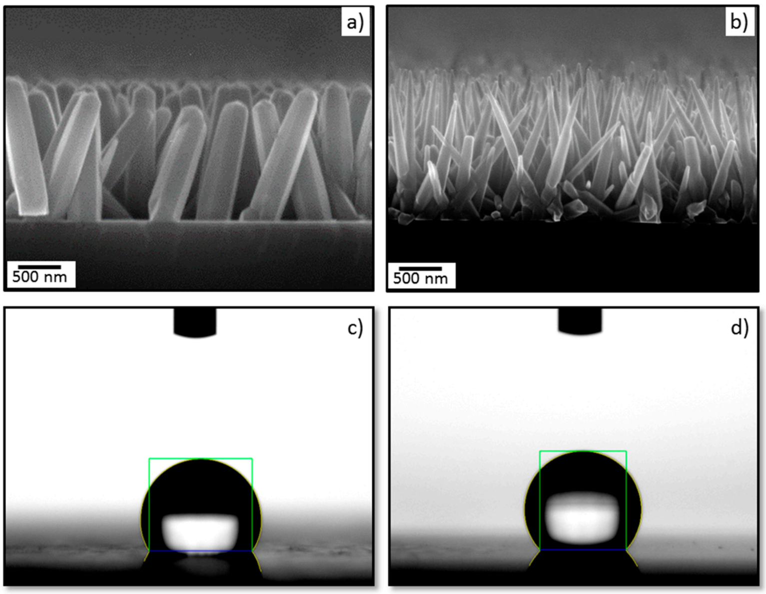

Figure 2. Cross-sectional SEM imaging of the ZnO rods (**a**) and needles (**b**), and their corresponding surface wetting behavior (contact angle of water droplets on the rods (**c**) and needles (**d**)).

Both rods and needles were integrated directly into the Si-based micromachined platforms via AACVD without pre-treatment of the platforms. Additional SEM and XRD of the as-deposited structures confirmed the integration of rods or needles with comparable characteristics to those deposited on the bare Si substrate, consistent with our previous reports on the fabrication of micromachined gas sensors based on other structured metal oxides (e.g., WO_3, SnO_2) integrated via AACVD [3,4]. Overall, the responses of the microsensors showed a reproducible and stable behavior, with the dependency of the response to hydrogen concentrations between 10 and 80 ppm showing power-law fitting curves. The resistance changes towards the exposure of these microsensors to 80 ppm of hydrogen and various RH atmospheres (from 10% to 80%) in dry air background are shown in Figure 3.

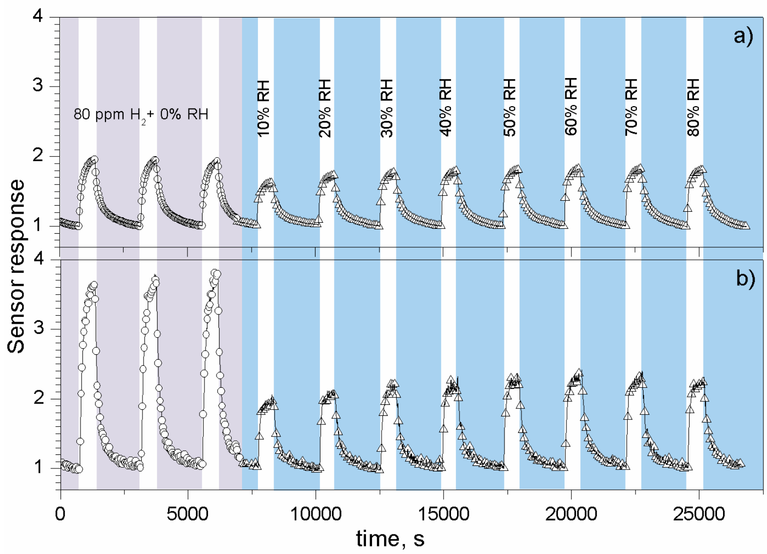

Figure 3. Film resistance changes recorded on the sensors based on ZnO rods (**a**) and needles (**b**) to either H_2 or various RH atmospheres in dry air background.

Results in Figure 3 demonstrate improved gas sensing properties to hydrogen for the microsensors based on needles as opposed to those based on rods, with the structures in the form of needles showing nearly two times more response than the structures in the form of rods; consistent with the higher-surface-to-volume ratio of the needles. These results also show negligible differences in the response to RH atmospheres for both structures (i.e., based on rods or needles) indicating lower humidity interference for the needles than the rods, in agreement with the higher hydrophobicity recorded on the surface coated with needles (Figure 2).

4. Conclusions

Columnar zinc oxide structures in the form of rods or needles with different aspect ratios and wetting properties were integrated into Si-based micromachined platforms. The gas sensing properties of these systems to hydrogen and humidity in dry air background demonstrated lower humidity-interference for the structures in the form of needles provided of higher hydrophobicity, as opposed to those in the form of rods, suggesting that the tuning of the wetting properties in metal oxides could allow for the humidity-resilient detection of gaseous analytes.

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Conflicts of Interest: The authors declare no conflict of interest.

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