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Shape-controlled ZnO nanostructures for gas sensing applications

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Abstract

In order to increase the sensitivity and selectivity of semiconducting gas sensors, we have integrated three different ZnO nanostructures as sensitive layers on silicon chips: cloudy-like nanoparticles, isotropic nanoparticles and nanorods. We have compared their response towards three gases, namely CO, C_3H_8, and NH_3. The morphology of ZnO nanostructures significantly influences the sensors responses to the reducing gases. These results demonstrate that sensor performance can be improved using the same sensitive material and by modifying only its shape this opens the way to new arrays of selective gas sensors.

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Keywords: ZnO ; gas sensors ; organometallic approach

1. Introduction

Shape controlled synthesis of inorganic materials at the nanometer scale has achieved much progress in the past decade. Among several attractive metal oxide materials studied so far, ZnO exhibits a wide variety of morphologies: nanoparticles, nanorods, nanotubes, nanowires, nanodisks, nanoneedles, and so on [1-5]. Each of these morphologies presents its own unique features in terms of size dispersion, surface properties, shape and organization, which have a crucial effect on their physical and chemical properties. Many examples have shown that the morphology of ZnO structure plays an important role when used as gas sensitive layers [1-3]. Hereafter we compare gas sensing properties of silicon based devices with three different ZnO morphologies as sensing layers, namely: cloud-like nanoparticles, isotropic nanoparticles and nanorods. All these nanostructures were prepared by a unique, one-pot, room-temperature organometallic approach. The method was developed in our team and is based on the controlled hydrolysis of metal-organic precursors in the presence of alkylamines [6, 7]. Sensors were exposed to different reducing gases, namely CO, C_3H_8, and NH_3 at various temperatures. The gas responses suggest that the morphology of ZnO nanostructures deeply influence sensor performance.

2. Materials and methods

2.1. Synthesis of ZnO nanostructures

Syntheses of ZnO nanostructures were performed at room temperature and under argon atmosphere in standard Schlenk tubes except for ZnO nanorods which were prepared in a flat-bottomed reactor. All nanostructures were prepared using the organometallic precursor ($[Zn(c\text{-}C_6H_{11})_2]$, NanoMePS). Octylamine (Sigma Aldrich) was used as stabilizing agent. THF was collected after going through drying columns (MB-SPS-800 solvent purification system) prior to use. Distilled water was degassed with argon during 30 min prior to use.

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ZnO isotropic nanoparticles were obtained from a THF (4 mL) solution of [Zn(c-C_6H_{11})$_2$] (0.25 mmol, 57.9 mg). Octylamine (0.25 mmol, 32.5 mg) was used as growth orienting agent. The hydrolysis was performed by addition of THF (2 mL) containing water (1 mmol, 18 µL). After 16 h the nanoparticles and solvent were separated by centrifugation and the nanoparticles were washed 3 times with 5 mL of acetone (Sigma Aldrich).

ZnO cloud-like nanoparticles were obtained following the same procedure but without octylamine.

ZnO nanorods were obtained following the same procedure but in the absence of THF. In the same time higher amount of octylamine was used (0.5 mmol, 65 mg) and the reaction time was longer (i.e. 4 days).

2.2. Transmission electron microscopy experiments

TEM specimens were prepared on carbon-supported copper grids. TEM images were obtained using a Hitachi 7700 microscope operating at 80 kV.

2.3. Sensors preparation

All freshly prepared and washed nanostructures were dispersed in ethanol (99.8 %, Sigma Aldrich). The concentration of the nanostructures in the solution was 5 mg.mL^{-1}. The solutions were then deposited on miniaturized gas sensors substrates [8], presented on Fig. 1, by an ink-jet method (Microdrop AG) [9].

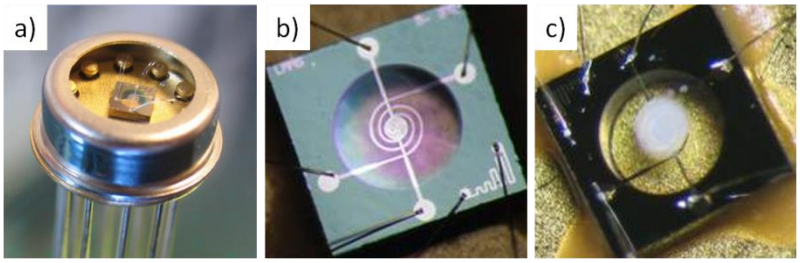

Fig. 1. Miniaturized gas sensor substrate (a), silicon platform before (b) and after (c) sensitive layer deposition

2.4. Gas test set-up

Gas tests were performed using a PC controlled setup composed of different gas bottles connected to mass flow controllers (QualiFlow) commanded by an Agilent Data Acquisition/Switch Unit 34970A. Sensors were placed in a specially designed measurement cell containing also the humidity and temperature sensors driven by another Agilent 34970A. The integrated sensor heater was commanded by a HP6642A tension controller. The NI 6035E electronic card established the connection between computer and measurements. Freshly prepared sensors were initially conditioned by a progressive *in situ* heating of the sensitive layers up to 500°C. Afterwards, all sensors were exposed to different reactive gases under 50% relative humidity and a total gas flow rate of 1L/min. The reported tests were performed at three different temperatures (500°C, 400°C and 340°C).

3. Results and discussion

Typical TEM images of the different ZnO nanostructures used in this study are presented on Fig. 2. Different reaction conditions (*Section 2.1.*) led to the formation of either cloudy-like nanoparticles, isotropic nanoparticles (diameter of *ca.* 5 nm), or nanorods (diameter of *ca.* 5 nm and length of *ca.* 20 nm). Sensors based on these ZnO nanostructures were exposed to different reducing gases in humid air conditions (RH 50%), namely 100 ppm CO, 100 ppm C_3H_8, and 19 ppm NH_3. Additionally, tests were performed at different temperatures: 500°C, 400°C and 340°C. Sensors responses, calculated as $S=(R_{air}-R_{gas})/R_{air}*100$, are presented on Fig. 3.

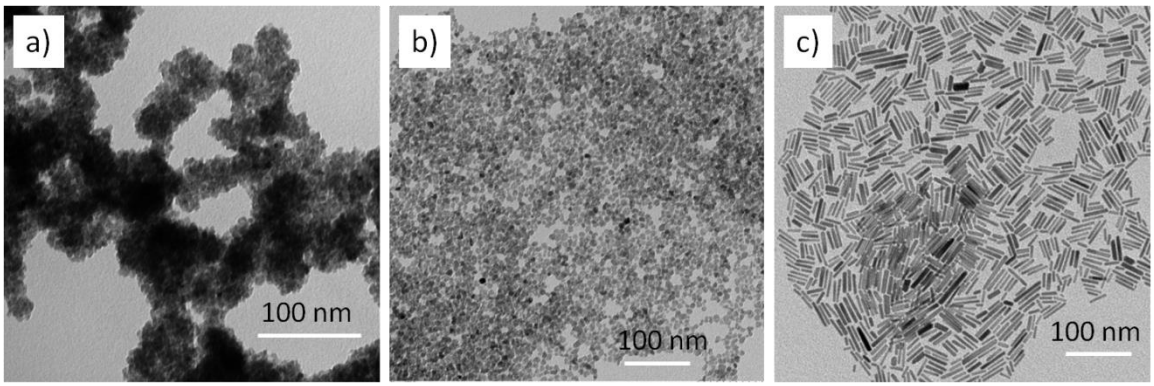

Fig. 2. TEM images of various ZnO structures: cloud-like nanoparticles (a), isotropic nanoparticles (b) and nanorods (c)

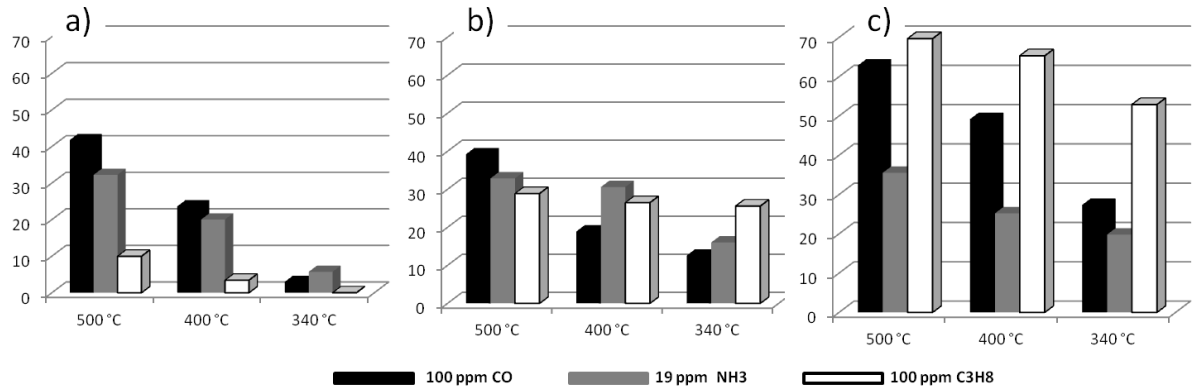

Fig. 3. Responses (%) of ZnO sensitive layers towards different gases; a) cloud-like nanostructures, b) isotropic nanostructures, c) nanorods

From all studied morphologies, ZnO nanorods gave the highest response toward CO at all tested temperatures. ZnO cloud-like nanoparticles and isotropic nanoparticles exhibited quite similar responses when exposed to this gas at higher temperatures (500°C and 400°C). However, at lower temperatures (340°C), ZnO cloud-like nanoparticles were less sensitive to CO than ZnO isotropic nanoparticles. Regardless of the morphology, a quite similar response to NH_3 was obtained for all ZnO sensors, but at lower temperatures, ZnO cloud-like nanoparticles showed the weakest response to this gas. Sensitivity of different ZnO based sensors towards C_3H_8 increases as follow: cloud-like nanoparticles, isotropic nanoparticles and nanorods. Temperature changes do not affect significantly the sensitivity toward this gas for sensors based on isotropic nanoparticles or nanorods. ZnO cloud-like nanoparticles gave very weak responses to C_3H_8 at all temperatures and almost no response at the lowest temperature (340°C). Thus, ZnO cloud-like layers appeared to be more sensitive to polar molecules such as CO and NH_3, whereas non polar C_3H_8 species have poor reactivity on this type of nanostructure. On the other side, when large crystalline faces are exposed to the gas (extended lateral faces of ZnO nanorods) the sensitivity to CO and propane is clearly enhanced. ZnO nanorods present a slightly higher sensitivity to propane compared to CO at 500°C. This sensitivity difference is even more increased when the sensor is operated at lower temperature, since the propane sensitivity stays around 50% at 340°C whereas CO one is lowered to 25%. These results highlight not only the role of the nanostructures morphology of the sensitive layer, but also the influence of temperature on gas sensor sensitivity and selectivity.

4. Summary

A reproducible organometallic approach was used in order to prepare zinc oxide gas sensitive layers. Various ZnO nanostructures with well-defined morphology were prepared and deposited on miniaturized gas sensors substrates by an ink-jet method. Sensors were tested at different temperatures towards three reducing gases, namely: CO, C_3H_8, and NH_3. We showed that the morphology of these nanostructures and the temperature significantly influences the sensor response level and the selectivity to the reducing gases.

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