Sensors and Actuators B 264 (2018) 249–254

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Suspended CoPP-ZnO nanorods integrated with micro-heaters for highly sensitive VOC detection

Kyounghoon Lee[a,1], Dae-Hyun Baek[a,1], Jungwook Choi[b], Jongbaeg Kim[a,*]

[a] School of Mechanical Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul, 03722, Republic of Korea
[b] School of Mechanical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan, Gyeongbuk, 38541, Republic of Korea

ARTICLE INFO

Article history:
Received 1 October 2017
Received in revised form 20 January 2018
Accepted 23 February 2018

Keywords:
VOC
Micro-heaters
ZnO nanorods
Gas sensors
Nanomaterials
Porphyrins
Functionalization

ABSTRACT

Suspended nanomaterials including nanowires and nanorods have attracted great interest as promising candidates for gas sensing materials because they can perform sensitive gas detection without being affected by the substrate. However, the suspended nanomaterial-based gas sensors reported so far have been developed in the absence of a heater, and given the fact that most sensors require high operating temperature, integration with the heater is essential for practical use of the sensor. This work demonstrates a suspended ZnO nanorod-based sensor integrated with a heater, based on a batch process. Depending on the degree of heating from the integrated heater, the suspended ZnO nanorods exhibited various sensitivities and the highest response was obtained when heated to 5.2 V. To further increase the response to volatile organic compounds (VOCs), the ZnO nanorods were functionalized with cobalt porphyrin and the functionalized ZnO nanorods exhibited response that was 2.6 times higher than that of the pristine one at 10 ppm toluene. The functionalized ZnO nanorods detected 2 ppb of toluene, which is lower than the concentration detectable by any of the previously reported chemoresistive VOC sensors.

1. Introduction

Harmful substances emitted from artificial materials such as artificial adhesives and paints used in interior building materials reduce the quality of the indoor air and pose a risk to human health [1–3]. Volatile organic compounds (VOCs) are one of the most important substances known to degrade indoor air quality. One of the typical effects of VOCs is the sick building syndrome (SBS). SBS is a condition that results from exposure to harmful chemical toxins at home or in the workplace. For this reason, many countries have enacted legislation to limit the VOC content. Further, various sensors have been developed to mitigate the damage caused by VOCs and to ensure a comfortable indoor environment. Exposure to even low concentrations of VOCs, especially BTEX (benzene, toluene, xylene, and ethylbenzene), in these places is dangerous and carcinogenic [4–7]. Therefore, it is very important to detect a low concentration of VOCs, especially in the range of ppb to less than ppm.

As a wide bandgap metal oxide semiconductor, Zinc oxide (ZnO) has attracted much attention as a chemical gas sensing material with high performance, low cost and environmentally friendly attributes [8–11]. However, because of low exposure to reactive crystal planes, and easy recombination of electron-hole pairs, traditional ZnO-based sensing materials still have low response to low concentration VOCs, which limits their practical application. Continuous efforts have been made to overcome these shortcomings, such as structure-controlling to form porous nanostructures to increase exposed sites, and improving the sensing properties by increasing the mobility and separation efficiency of the electron-hole pairs [12–17]. Nonetheless, even these improved ZnO-based sensors still have limits in sensing performance for low concentration VOC gases, such as undetectable response for sub-ppb level concentration or significant drift of sensing signals. Therefore, it is highly desirable to develop a highly sensitive gas sensor capable of detecting VOC gas at very low concentration, especially at the ppb level.

Meanwhile, studies have been conducted to increase the response of the 1D nanomaterial-based sensors, and as a result, it has been found that more sensitive gas detection is possible when the sensing materials are present in a suspended form [18–24]. Suspended nanomaterials are less susceptible to noise or influence from the substrate than the nanomaterials attached to the substrate and can also escape from the boundary layer formed due to gas stagnation near the substrate, allowing more sensitive gas detection. Various suspended 1D nanomaterials such as functionalized tung-

* Corresponding author.
E-mail address: kimjb@yonsei.ac.kr (J. Kim).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.snb.2018.02.161
0925-4005/

sten nanowires [18], carbon nanotubes [19], GaN nanowires [20], and Pd-carbon nanowires [21] have been used as gas sensing materials for sensitive gas detection. However, all the above-mentioned sensors were developed without heater integration, which is a large factor preventing practical use of the gas sensor, considering that most gas sensors require a high temperature at the time of sensing.

We developed a suspended ZnO nanorod-based gas sensor for detecting low concentration of VOCs. Unlike conventional suspended 1D nanomaterial-based sensors, the suspended nanorods are integrated with a heater platform, which can be utilized in normal environment (not in high temperature furnace), because the operating temperature can be adjusted at low power without any additional external heat source [19,20,23]. All fabrication processes, including the micro-electro-mechanical systems (MEMS) process for the heater-integrated sensor platform, and the growth of the suspended ZnO nanorods, consisted of batch-processes. To detect low concentration of VOCs by improving the response of the suspended ZnO nanorod-based gas sensor, porphyrin was used as a functional material. Porphyrins are known to provide more adsorption sites for VOCs and enable more sensitive detection of VOCs [25–28]. Among the various porphyrins, we chose cobalt porphyrin (CoPP), which is reported as the most efficient element for electrocatalytic reduction of oxygen ions used for VOC sensing [29].

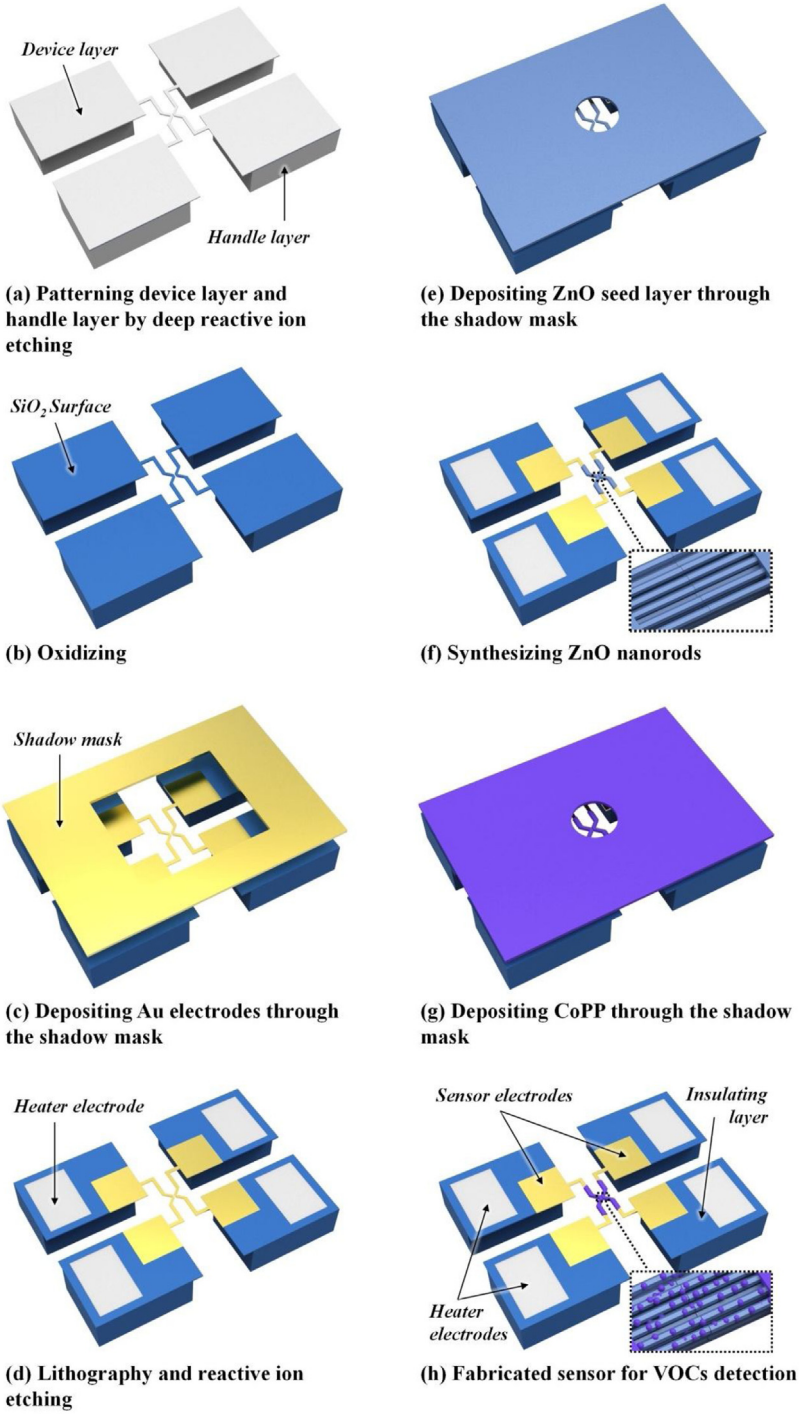

Fig. 1. Schematic diagram showing fabrication process for the heater-integrated VOCs sensor.