ARTICLE IN PRESS

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International ▮ (▮▮▮▮) ▮▮▮–▮▮▮

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

NO_2 gas sensing properties of Au-functionalized porous ZnO nanosheets enhanced by UV irradiation

Youngho Mun[a], Sunghoon Park[a], Soyeon An[a], Chongmu Lee[a,*], Hyoun Woo Kim[b]

[a]Department of Materials Science and Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
[b]Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

Received 21 February 2013; received in revised form 10 April 2013; accepted 10 April 2013

Abstract

Porous ZnO nanosheets were synthesized by thermal evaporation. The morphology, crystal structure, and sensing properties of the ZnO nanosheets to NO_2 gas at room temperature under UV illumination were examined. Au nanoparticles with diameters of a few tens of nanometers were distributed over the ZnO nanosheets. The responses of the multiple networked nanosheet gas sensors were improved 1.8–3.3 fold by Au functionalization at NO_2 concentrations ranging from 1 to 5 ppm. Furthermore, the Au-functionalized ZnO nanosheet gas sensors showed a considerably enhanced response at room temperature under ultraviolet (UV) illumination. In addition, the mechanisms through which the gas sensing properties of ZnO nanosheets are enhanced by Au functionalization and UV irradiation are discussed.

Keywords: D. ZnO; Au; Functionalization; Gas sensing; Nanosheet

1. Introduction

ZnO is a functional material that is sensitive to toxic and combustible gases [1]. ZnO gas sensors with a range of structures, such as powders [2], thin films [3], heterostructures [4], nanoparticles [5], and one-dimensional nanostructure [6] have been demonstrated. Among these nanostructures, one-dimensional (1D) ZnO nanostructures are particularly useful because of their large length-to-diameter ratio and large surface-to-volume ratio. Studies of the gas sensing properties of ZnO 1D nanostructures focused mainly on CO, H_2S, HCHO, NH_3, H_2, ethanol and humidity [7], whereas there are limited reports on the NO_2 sensing properties of ZnO 1D nanostructures (Table 1) [8–12]. In particular, Zhang et al. compared the sensing properties of brush-like hierarchical ZnO nanostructures to many different types of gases with those of the straight ZnO nanowires [8]. They reported that the brush-like hierarchical ZnO nanostructures exhibited approximately 1.5 fold stronger responses to ethanol and C_6H_6 gases than straight ZnO nanowires, but showed similar responses to the other gases. Regarding the response of ZnO nanostructures to NO_2 gas, the sensitivity of ZnO fiber-mats was reported to be more than 100 toward NO_2 at room temperature [13]. The fiber-mat structure showed an order of magnitude stronger response compared to the cauliflower structure. The difference between the sensing properties of these two structures can be attributed to the differences in their morphologies, because the fiber-mats have more surface available for reaction than the cauliflower structure.

Despite the enhanced gas sensing properties of 1D nanostructures compared to thin films, enhancing their sensing performance and detection limit is still a challenge. A range of techniques such as surface functionalization with novel metals including Pd, Pt and Au [14–17] or doping with novel metals [18–20], MEMS fabrication [21], nanosensing materials [22], application of electrostatic field [23], and ultraviolet (UV) irradiation [24–32] have been developed to reduce the operating temperature and improve the sensitivity and stability of 1D nanostructure-based sensors. Among these techniques, the functionalization of nanowire surfaces with catalyst such as Pd and Pt may be the simplest and most effective technique because the resistance of the sensor changes considerably upon exposure to target gas at room temperature. The optical and electrical properties of the 1D nanostructures coated with catalyst can change upon exposure to gas and can be restored

*Corresponding author. Tel.: +82 32 860 7536; fax: +82 32 862 5546.
E-mail address: cmlee@inha.ac.kr (C. Lee).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.04.035

Please cite this article as: Y. Mun, et al., NO_2 gas sensing properties of Au-functionalized porous ZnO nanosheets enhanced by UV irradiation, Ceramics International (2013), http://dx.doi.org/10.1016/j.ceramint.2013.04.035

Table 1
Comparison of Au nanoparticles in the Au-functionalized ZnO nanosheets prepared in this study with those in previous studies.

Nanomaterial	Au particle size (nm)	Annealing temperature (°C)	NO_2 concentration (ppm)	Response (%)	Reference
ZnO nanosheets	10–50	700	5	455	Present work
ZnO nanorods	5	–	5	200	[33]
SnO_2 nanowires	20–100	–	10	400	[34]
In_2O_3 thin films	20–30	600	10	140	[35]
CNT	10–40	200	10	110	[36]

upon reexposure to air even at room temperature [14–20]. Such low temperature-processes are desirable for detecting toxic gases safely. UV irradiation is another simple and effective technique. Over the past decade, many studies have shown that UV irradiation improves the sensing performances of semiconducting oxide gas sensors [24–32]. On the other hand, although there have been many reports on the gas sensing properties of one-dimensional nanostructures UV illumination, few studies have examined those of one-dimensional nanostructures functionalized with metal catalyst under UV illumination. This study examined the NO_2 gas sensing properties of multi-networked porous ZnO nanosheets functionalized with Au at room temperature under UV illumination to identify the practical use of ZnO-based gas sensors at room temperature.

2. Experimental

Au-functionalized ZnO nanosheets were synthesized using a three-step process: the synthesis of ZnO nanosheets by the thermal evaporation of Zn powders followed by the sputter-deposition of Au and thermal annealing. First, Au-coated sapphire was used as a substrate for the synthesis of ZnO nanosheet structures. A ~3 nm thick Au thin film was deposited on the (0001) sapphire substrate by direct current (dc) sputtering. A quartz tube was mounted horizontally inside a tube furnace. The 99.99% pure Zn powder was placed on the lower holder at the center of the quartz tube. The Au-coated sapphire substrate was placed on the upper holder approximately 5 mm apart from the Zn powder. The furnace was heated up to 700 °C and maintained at that temperature for 1 h in N_2/3 mol%–O_2 atmosphere with constant flow rates of oxygen (O_2) (3 sccm) and N_2 (100 sccm). The total pressure was set to 1.0 Torr. For the second stage, Au thin film was deposited on the surfaces of some of the as-synthesized ZnO nanosheet samples by direct current (dc) sputtering (substrate temperature: room temperature, power: 20 mA, working pressure: 1.9×10^{-2} Torr, and process time: 100 s). Subsequently, the Au-coated nanosheets were annealed at 700 °C for 1 h in air.

The collected nanosheet samples were characterized by scanning electron microscopy (SEM, Hitachi S-4200), transmission electron microscopy (TEM, Philips CM-200) equipped with an energy-dispersive X-ray spectrometer (EDS) and X-ray diffraction (XRD, Philips X'pert MRD diffractometer). The crystallographic structure was determined by glancing angle XRD using Cu K_α radiation (0.15406 nm) at a scan rate of 2°/min. The sample was arranged geometrically at a 0.5° glancing angle with a rotating detector.

For the sensing measurements, Ni (~10 nm in thickness) and Au (~50 nm) thin films were deposited sequentially by sputtering to form electrodes using an interdigital electrode (IDE) mask. Multiple networked Au-functionalized ZnO nanosheets gas sensors were fabricated by pouring a few drops of nanosheet-suspended ethanol onto oxidized Si substrates equipped with a pair of IDEs and a gap length of 20 μm. The electrical and gas sensing properties of the pristine ZnO nanosheets and Au-functionalized ZnO nanosheets were measured using a home-built computer-controlled characterization system consisting of a test chamber, sensor holder, Keithley sourcemeter-2612, mass flow controllers and a data acquisition system. During the measurements, the nanosheet gas sensors were placed in a sealed quartz tube with an electrical feed through. The test gas was mixed with dry air to achieve the desired concentration, and the flow rate was maintained at 200 sccm using mass flow controllers. The working temperature of the sensors was adjusted by changing the voltage across the heater side. The gas sensing properties of the Au-functionalized ZnO nanosheets were measured at room temperature in a quartz tube placed in a sealed chamber with an electrical feed through. The sensor test was performed by measuring the resistance of the sensor upon controlled concentration of NO_2 gas in the dark and under UV (λ=365 nm) illumination at 1.2 mW/cm^2. The response of the Au-functionalized ZnO nanosheets is defined as R_g/R_a for NO_2, where R_a and R_g are the electrical resistances in the sensors in air and target gas, respectively.

3. Results and discussion

Fig. 1 shows a SEM image of the Au-functionalized ZnO nanosheets synthesized in this study. The synthesis scheme adopted in this study can grow equilateral triangular shaped ZnO nanosheets with a mean base and height of ~0.5 μm and ~1 μm, respectively. The ED spectra obtained by focusing on Au nanoparticle (Fig. 2(a)) and on the ZnO nanosheet (Fig. 2(b)) in Au-functionalized ZnO nanosheet confirmed that the Au-functionalized ZnO nanosheet was composed of Zn, O and Au. The Cu and C in the spectrum were attributed to the TEM grid. The EDS elemental map (Fig. 2(c)) of a typical Au-functionalized ZnO nanosheet showed that Au nanoparticles were distributed sparsely over the surface of the ZnO nanosheet.

The low-magnification TEM image (Fig. 3(a)) shows a typical Au-functionalized ZnO nanosheet. Black and white particles with various sizes were observed on the nanosheet. The white round particles are not real particles but pores, whereas the black round particles are Au nanoparticles. Therefore, the ZnO nanosheet is porous. The diameters of the Au particles ranged from 10 to 50 nm. Table 1 compares

Please cite this article as: Y. Mun, et al., NO_2 gas sensing properties of Au-functionalized porous ZnO nanosheets enhanced by UV irradiation, Ceramics International (2013), http://dx.doi.org/10.1016/j.ceramint.2013.04.035