HIGHLY INTEGRATED SNO_2 NANOTUBES USING TEMPLATED ZNO NANOWIRES FOR LOW POWER GAS SENSORS

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ABSTRACT

We have developed highly sensitive, low power gas sensors consisting of beam-shaped, suspended microheaters and locally synthesized 1-D metal oxide nanostructures. In-situ localized hydrothermal synthesis method was utilized to grow ZnO nanowires on the Joule-heated region. Also, liquid phase deposition (LPD) process enabled to formulate SnO_2 thin film on the surface of ZnO nanowires and to etch ZnO out at the same time. Therefore, we could fabricate highly integrated and sensitive SnO_2 nanotubes on the selective region less than 50^2 μm^2. Due to the small and suspended heating area, operating power of the gas sensor was less than 10 mW at 300 ℃. Also, the sensitivity (R_{air}/R_{gas}) of SnO_2 nanotubes for H_2S gas was around 6 times larger than that of pre-processed ZnO nanowires.

INTRODUCTION

Nowadays, because air pollution is a critical problem, many types of portable air monitoring devices have been developed. Semiconductive metal oxide (SMO) gas sensors are suitable for mobile applications due to their small size, low cost and high sensitivity. However, they usually need high operation temperatures ranging from 200 ℃ to 400 ℃, requiring high electrical power for heating. In order to reduce the operating power, researchers have tried to combine micro-heating platforms and sensing nanomaterials. Most widely used approaches are based on drop casting or printing (e.g. inkjet printing, screen printing etc.) of pre-synthesized nanomaterial through CVD, PVD and sol-gel methods. These methods are simple and highly productive. However, they require additional dispersion process of nanomaterials in liquid solvent and have limitation of downscaling. For example, Zhou et al. developed ultra low power microheaters which require only 2 mW of power at 300 ℃ for SMO gas sensors [1]. They developed a beam-shaped suspended structure to isolate the heating spot as well as a quite small dimension - 2 μm width and 100 μm length. However, previously mentioned deposition methods do not allow fine integration of sensing nanomaterials on such a small selected areas, except for a form of thin film. Meanwhile, Long et al., and Xu et al introduced a direct synthesis method of porous SnO_2 films on microheating platforms using an explosive evaporation method and a polystyrene (PS) bead-templated method, respectively [2-3]. Although nano-scale sensing materials on microheaters were well formulated, there were limitations in applying on a suspended microstructure or a highly small area.

This paper introduces novel integration method of 1-D nanomaterials on miniaturized microheaters to achieve both high sensitivity and low power operation. The suspended structure of microheaters can thermally isolate the heating spot from bulk Si substrates. It dramatically reduces heat loss to the substrate, resulting in low power gas detection. Also, we directly synthesized ZnO-templated SnO_2 nanotubes on suspended microheaters in a low cost, fast and low-temperature liquid-phase process. Yang et al. reported a localized hydrothermal synthesis method for ZnO nanowires [4]. When electrical voltage is applied on the pre-fabricated microheaters dipped in the ZnO precursor, the temperature rise around localized Joule-heated regions induce a hydrothermal reaction of precursor chemicals. Also, as convective heat and mass transfers of ZnO precursor are generated, fresh precursors are continuously supplied to the reaction area. Based on this method, ZnO nanowires could be grown on the desired spots. In order to enhance gas sensing performances, we substituted pre-synthesized ZnO nanowires for the SnO_2 nanotubes via liquid phase deposition (LPD) process because SnO_2 is well known for its highly sensitive, chemically and thermally stable gas-sensing material. LPD process formulated a SnO_2 thin film on the surface of ZnO nanowires. Due to the acidic condition of the LPD solution, ZnO nanowires were etched out simultaneously (Figure 1). Synthesized SnO_2 nanotubes were gas-permeable due to the surface pores that precursor solution passed through. This method allows facile integration of sensing nanomaterials on selective microscale spots, which is difficult when using other conventional deposition methods. Due to the small and suspended heating area, operating power of the gas sensor at 300 ℃ was less than 10 mW. Also, the gas sensing performance of the fabricated sensors was demonstrated by measuring their sensitivity to toxic gas - H_2S.

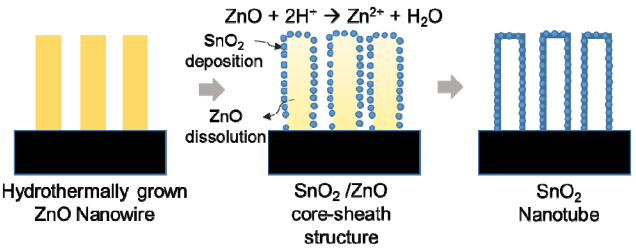

Figure 1: Schematic of the steps for forming the end-closed SnO_2 nanotubes.

EXPERIMENTAL METHODS

Design and Fabrication of Microheaters

Suspended beam shaped microheaters were designed to achieve low power operation. Total length of the beam was 200 μm and width of the beam was 50 μm. On the center of the beam, the coil-shaped Pt microheater was located within

50 μm region for focused heating. Then, the interlayered SiO_2 insulation layer and top Au electrodes were sequentially deposited. Designed microheaters were prepared through conventional MEMS processes using Si substrates such as photolithography, plasma-enhanced chemical vapor deposition (PECVD) of SiO_2 layers, e-beam deposition of metal layers (Pt, Au) and Tetramethylammonium hydroxide(TMAH) bulk etching. Finally, as seeds to grow ZnO nanowires, ZnO nanoparticles were deposited by sputtering (100 W, 3 min) on fabricated microheaters.

The temperature distribution of the Joule-heated region in liquid precursor was estimated by numerical simulation (Joule heating, heat conduction, convective flow models in COMSOL Multiphysics®) to verify the area occurring hydrothermal reactions. Also, a relationship between heating power and temperature in atmosphere was measured via the resistive temperature detection (RTD) method to estimate the operating power as a gas sensor.

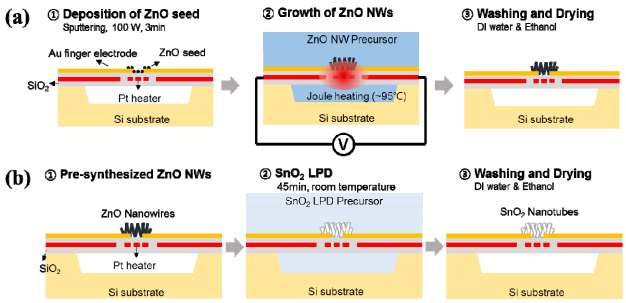

Figure 2: Fabrication Processes: (a) Localized synthesis of ZnO nanowires and (b) substitution to SnO_2 nanotubes through LPD.

Synthesis of ZnO Nanowires and SnO_2 Nanotubes

Whole processes to synthesize SnO_2 nanotubes are illustrated in Figure 2. First, Fabricated microheaters were dipped into the ZnO precursor prepared by dissolving zinc nitrate hydrate 25 mM, hexamethylenetetramine(HMTA) 25 mM, polyethyleneimine(PEI) 6 mM in DI water. As microheaters heated up to 95 ℃ for 30 min, ZnO nanowires grew only on Joule-heated region. To avoid failure of suspended microheater during drying process, ethanol which has low surface tension (22.1 mN/m at 20 ℃) was utilized in final rinsing and drying process.

Second, after washing and drying, synthesized ZnO nanowires were substituted to SnO_2 nanotubes by dipping in LPD precursor (SnF_2 15 mM, HF 60 mM, H_2O_2 30 mM and H_3BO_3 150 mM in DI water) for 45 min in room temperature [5]. In order to control the etching rate of ZnO, initial pH level was controlled to 4 by adding NaOH 1 M. After finishing whole processes, samples were washed and dried by using ethanol as before.

Measurement of Gas Concentration

The gas sensing performance of the fabricated sensors was demonstrated by measuring their sensitivity to H_2S gas for various operating power. (6, 8 and 10 mW). 1 to 20 ppm of H_2S gas was supplied in to the chamber by balancing the flow rates of air and H_2S gas. An electrical power for the microheater was applied by using a DC power supply (E3642A, Agilent) and the resistances of three sensing materials were simultaneously measured by a source meter (2400, Keithley).

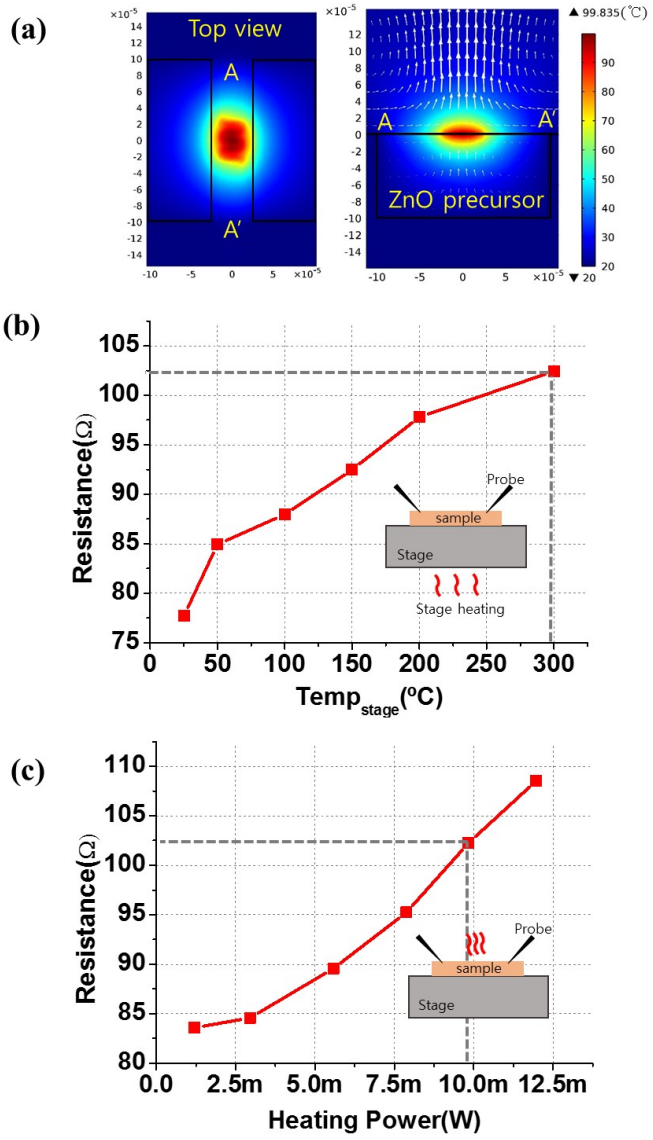

Figure 3: (a) Results of Numerical simulation for temperature distribution of the microheater in the precursor (left = top view, right = cross-sectional view), (b),(c) Results of resistive temperature detection

RESULTS AND DISCUSSION

Power Consumption of Microheaters

Figure 3a shows results of numerical simulation for temperature distribution of microheater in the precursor. The area which has temperature larger than 90 ℃ was well focused on the center of the microheater. Also, convective flows of precursors were generated from the local hot spot,

resulting in continuous supplement of fresh precursors.

We measured the heating power of microheater in atmospheric state through the RTD method. Graphs in Figure 3b and c represent the resistance change of the microheater as heating a hot chuck under the sample and as heating the microheater by the Joule heating, respectively. Comparing these relationship among temperature, electrical resistance and applied heating power, we could estimate that approximately 10 mW of heating power was need to reach 300 ℃.

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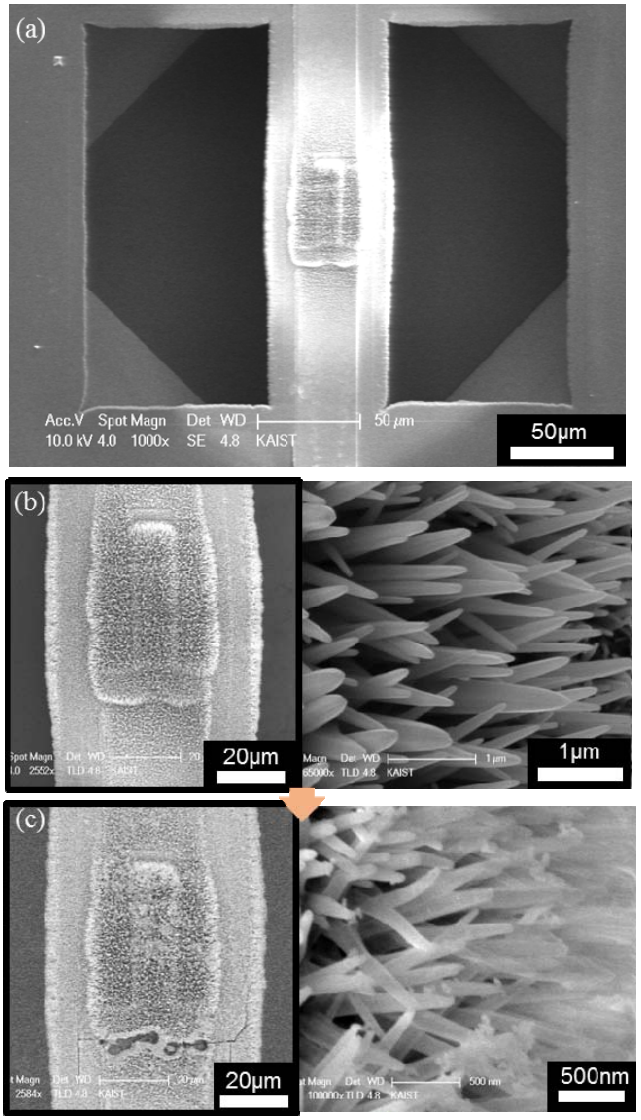

Figure 4: SEM image of (a) beam-shaped suspended microheater and synthesized ZnO nanowires on Joule-heated area, (b) Bare ZnO nanowires before LPD and (c) SnO_2 nanotubes after LPD on the suspended microheater.

Material Characterization

As shown in Figure 4a, beam-shaped suspended microheaters were fabricated and ZnO nanowires were intensively grown on heated region of microheater. The diameter of ZnO nanowires ranged from 40 nm to 200 nm, and their lengths ranged from 1 μm to 3 μm. After LPD of SnO_2, core ZnO were etched out due to acidic condition of LPD precursor. Therefore, translucent and hollow tubular structure was well formulated (Figure 4b and c).

In order to observe more detailed morphology of synthesized SnO_2 nanotubes and effect of LPD processing time, we diversified the LPD processing time ranged from 15 min to 45 min at intervals of 15 min and carried out TEM and EDS analysis. As shown in Figure 5a-c, the thickness of SnO_2 shell increased from 6-7 nm to 12-14 nm as processing time increased. Also, from the EDS spectra shown in Figure 5d and e proportion of Zn decreased while proportion of Sn increased. Tubular structure and EDS results indicate ZnO nanowires were partially removed during conversion process.

Sensor Performance

The gas sensing performance of the fabricated sensors was demonstrated by measuring their sensitivity to H_2S gas under various operating power (6, 8 and 10 mW). Corresponding temperature was expected to be 150, 200 and 300 ℃ from the RTD data. Figure 6a and b represent dynamic responses of bare ZnO nanowires and SnO_2 nanotubes at different heating powers. From the summary of sensitivity (R_{air}/R_{gas}) shown in Figure 6c, the sensitivity of SnO_2 nanotubes were around 6 times larger than that of bare ZnO nanowires for each operating power. (eg. R_a/R_g=22 for SnO_2 vs. R_a/R_g =3.9 for ZnO to 10 ppm H_2S at 10 mW of operation power) Also, 80 % response time of SnO_2 nanotubes was less than 30 sec for the whole ranges of heating power (Figure 6d).

Enhanced sensing performance of SnO_2 nanotubes could be explained by their increased surface to volume ratio and heterojunction effect of SnO_2 and residual ZnO inside SnO_2 nanotubes [6].

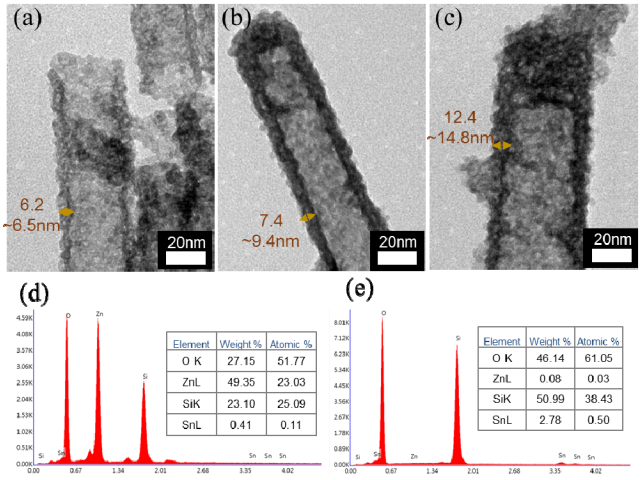

Figure 5: TEM images of SnO_2 nanotubes after LPD for (a) 15 min, (b) 30 min and (c) 45 min. EDS spectra of (d) bare ZnO nanowires and (e) SnO_2 nanotubes after LPD for 45 min.

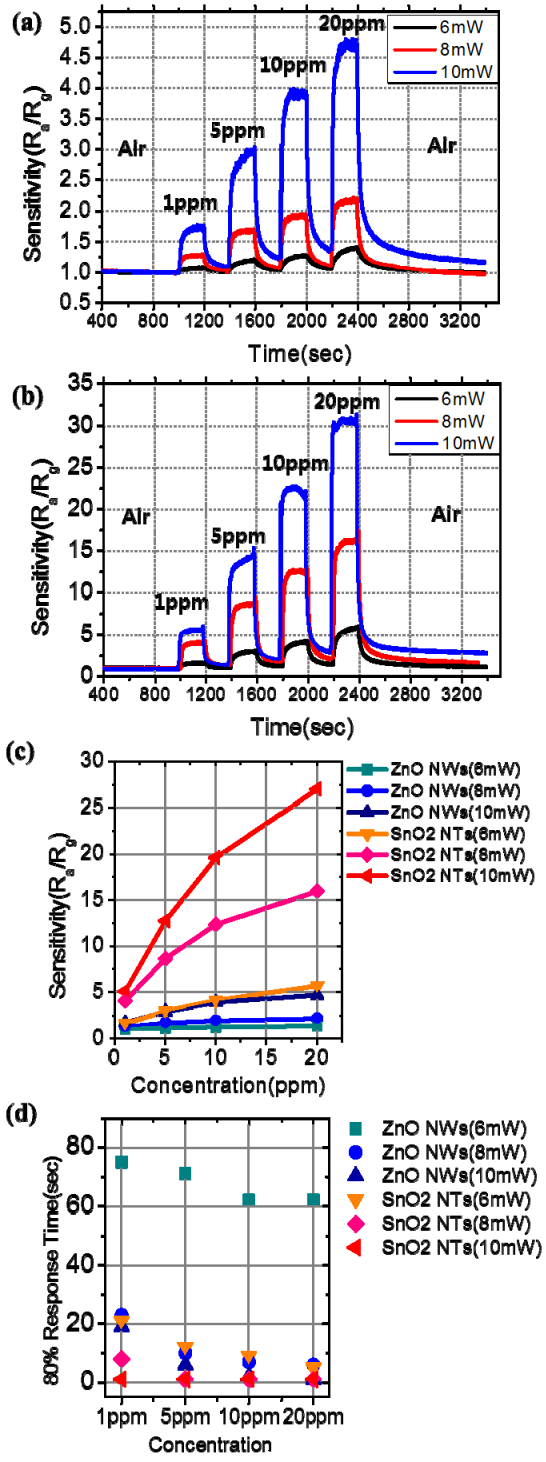

Figure 6: Results of H_2S gas sensing test : (a) Response of bare ZnO nanowires. (b) Response of SnO_2 nanotubes. (c) Summary of Sensitivity (R_a/R_g) vs. gas concentration for whole sensing material and heating power. (d) 80 % response time of ZnO nanowires and SnO_2 nanotubes to each gas concentration at different heating powers.

CONCLUSION

In summary, we found the novel synthesis method of SnO_2 nanotubes using ZnO nanowire templates. This method enables the fabrication of SnO_2 nanotubes within sub-50μm region on suspended microheaters. Therefore, the operating power was less than 10 mW and the sensitivity of SnO_2 natotubes to toxic gas (H_2S) was around 6 times larger than pre-processed ZnO nanowires. As a conclusion, proposed methods could achieve the high performance gas sensor which has both high sensitivity and low power operation through low cost, fast and low-temperature liquid-phase process.

ACKNOWLEDGEMENTS

This work was supported by the Center for Integrated Smart Sensors funded by the Ministry of Science, ICT & Future Planning as Global Frontier Project (CISS-2011-0031870) and Basic Science Research Programs (No. 2015R1A5A1037668) through the National Research Foundation (NRF) funded by the Korean government and the 'Development of Management Technology for HNS Accident' funded by the Ministry of Oceans and Fisheries, Korea.

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