HIGHLY SENSITIVE NO_2 GAS SENSOR BASED ON ZINC OXIDE/COPPER OXIDE HYBRID-NANOSTRUCTURES

M. K. Fuadi[1], D. Yang[1], C. Park[2], and I.Park[1]*
[1]School of Mechanical, Aerospace, and Systems Engineering,
Korea Advanced Institute of Science and Technology (KAIST), Daejeon, SOUTH KOREA
[2]Dept. of Materials Science and Engineering,
Korea Advanced Institute of Science and Technology (KAIST), Daejeon, SOUTH KOREA

ABSTRACT

This work explains a facile approach to fabricate hybrid-nanostructure based gas sensor. The prefabricated sensor chip with microheaters was used to grow ZnO/CuO hybrid-nanostructures directly on top of electrodes using hydrothermal reaction at low temperature (<95 °C). It was found that controlling the precursor concentration and growth time were the keys to minimize the damage on the base structures. As a gas sensor, the fabricated device based on ZnO/CuO hybrid-nanostructures was tested and shown to enhance the response from 2500 to 7100 % as compared to the ZnO nanowire-based device upon the exposure to 20 ppm of NO_2 gas at 250 °C.

KEYWORDS

Hybrid-nanostructures, metal oxide gas sensor, hydrothermal synthesis, Joule heating, MEMS

INTRODUCTION

In recent years, metal oxide nanostructures gained great attention from researchers because of their superior sensing performances including sensitivity and response time compared to their bulk structures. Many reports [1-3] have shown nanostructured materials such as nanotubes, nanowires, nanoparticles, and nanobelts have superior results due to their higher sensitivity and selectivity to certain gaseous species. Gas sensing properties of various individual materials have been explored intensively using SnO_2, ZnO, and In_2O_3 materials as n-type semiconductors.

Many attempts were presented to enhance the sensitivity by introducing noble metal nanoparticles. By means of spill-over effect or catalytic effect, the sensitivity can be improved significantly. Various noble metals such as Au, Pt, and Pd were found to be efficient for increasing the sensitivity to H_2 gas using WO_3 nanowires [4], to NO_2 gas using ZnO nanowires [5], and to H_2 gas using SnO_2 nanowires [6], respectively. However, in the real applications, such noble materials require high cost so that the sensor price can be high.

Alternatively, hybrid structures of nanomaterials were proposed to enhance sensitivity with its unique properties so that the sensor price can be lowered without sacrificing the sensing performances. Generally, hybrid nanostructure-based gas sensors can be made by using nanowires or nanoribbons as base materials and coating distributed nanoparticles or smaller nanostructures on the base materials resulted in branch-like structures. Many researchers believe that sensitivity and selectivity of sensor may be enhanced by combining two nanostructures with different electronic properties [7-9]. As further expectation, the hybrid nanostructures can be listed as a new class of nanomaterials with different properties. Here, we demonstrated gas sensor based on ZnO/CuO hybrid-nanostructures made through all solution-based precursors grown at relatively low temperature with enhanced sensitivity at lower operating temperatures. In addition, this method may provide simpler and faster fabrication compared with previous works [7-8].

FABRICATION

The fabrication process was started by manufacturing the sensor platform that consists of gold sensing electrodes and platinum microheaters using photolithography technique. As illustrated in Figure 1, silicon substrate with oxide was patterned by using photoresist (PR) to make microheater pattern. Then very thin layer of chrome as an adhesive layer and platinum layer were deposited subsequently. As an insulation layer, silicon oxide was covered by using LPCVD process. Finally, another PR layer was patterned to make inter-digitated sensing electrodes before deposition of gold layer. The gap distances between adjacent electrodes were maintained at 4 μm.

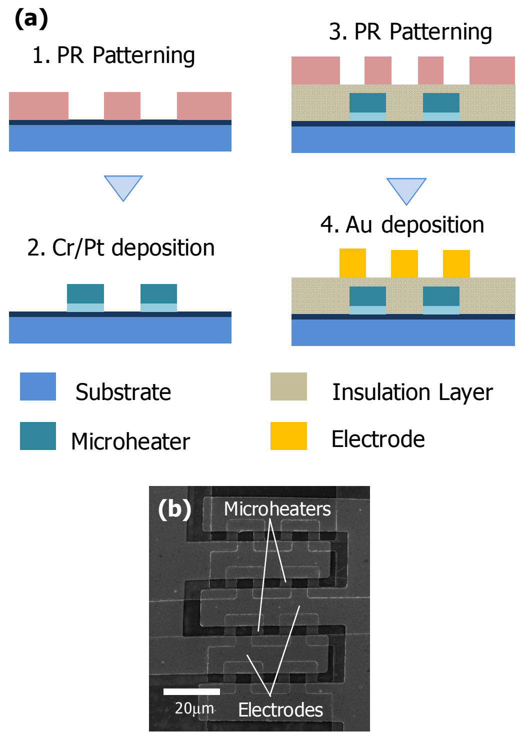

Figure 1: (a) Chip fabrication process using photolithography, and (b) SEM images of sensing electrodes and microheaters pattern.

To synthesize hybrid-nanostructures, the seed layer of ZnO nanoparticles was firstly coated on top of sensing platform by precipitating zinc acetate-based solution using ethanol at 150°C for 20 min. Then, ZnO nanowires (NW) were grown from nitrate-based solution using localized hydrothermal technique by addressing sufficient heat (approx. 95°C) via microheaters for 30 min. The heat source was generated through localized Joule heating by flowing current of DC power supply at 2 V. Another seed layer was introduced on top of ZnO NW by similar manner. Lastly, CuO nanostructures (NS) were grown directly on ZnO NW surfaces at 95°C using previous procedure for 30 seconds. CuO precursor was made by mixing $Cu(NO_3)_2 \cdot 3H_2O$ and hexamethylenetetramine (HMTA) in DI water. Different CuO precursor concentrations (4 and 0.25 mM) were used to be compared. Schematically, overall synthesis process is shown in Figure 2.

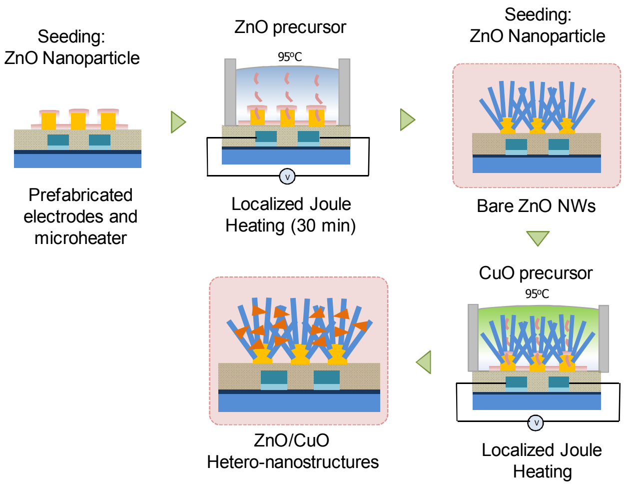

Figure 2: Synthesis process of ZnO/CuO hybrid-nanostructures using localized Joule heating via microheaters.

EXPERIMENTAL

The gas sensing measurement was conducted by using a quartz tube furnace at various temperatures. Total gas flow rate was maintained at 600 sccm by using a mass flow controller. The resistance of sensor was measured by using a sourcemeter (*Keithley 2400*). The sensor response was defined as relative sensitivity $S = (R_{gas} - R_{air})/R_{air} \times 100\%$. As a preliminary test, 20 ppm of NO_2 was introduced. The same sensor sample was used for the gas testing before and after growing CuO nanostructures on ZnO nanowires.

RESULTS AND DISCUSSION

In Figure 3 (a-b), SEM images of bare ZnO NW and hybrid-nanostructures of ZnO NW/CuO NS were recorded from the same location. It was clearly shown that CuO NS were successfully synthesized and equally distributed throughout the ZnO NW using low concentration of CuO precursor (0.25 mM) for 30 seconds. In Figure 3 (c), a close-up look of CuO NS could be obtained. Its dimension ranged from 240-270 nm in length and 40-50 nm in width with sharp tip feature.

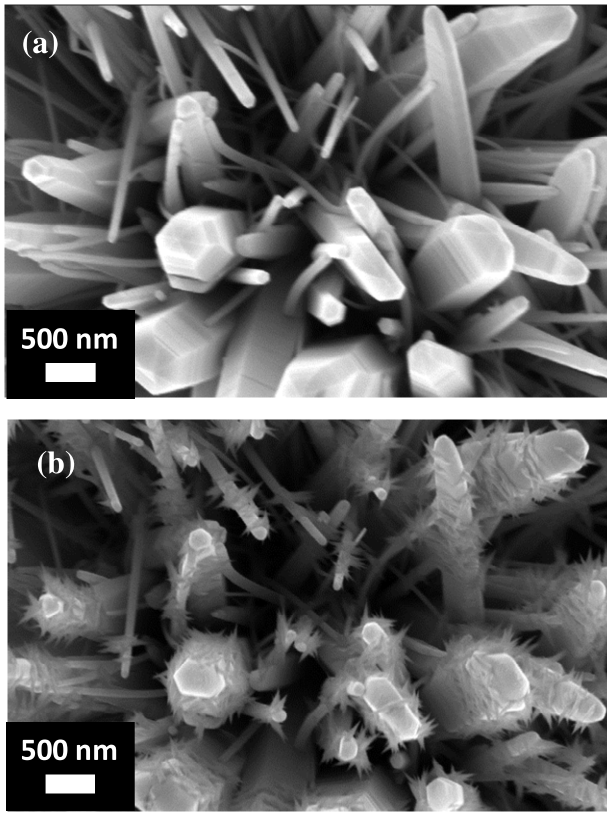

Figure 3: SEM images of (a) bare ZnO NW and (b-c) ZnO NW/CuO NS using 0.25mM precursor of CuO.

Elemental mapping of Zn and Cu were displayed using STEM-EDS images on Figure 4. It could be simply observed that the hybrid-nanostructures were well synthesized. Even at high level of Cu noise due to TEM grid, the Cu element on CuO NS part was slightly shown denser than its background.

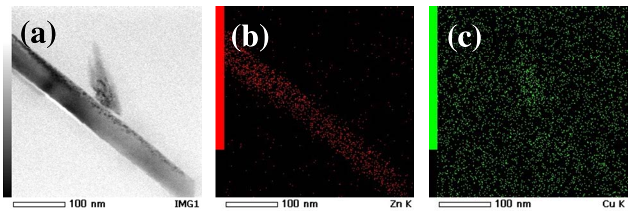

Figure 4: STEM image of (a) ZnO NW/CuO NS, and EDS mapping images of (b) element of Zn, and (c) element of Cu.

On the other hand, using 4 mM of CuO precursor concentration for five minutes, it can be seen that rapid reaction of CuO formation damaged the ZnO NW that some parts of NW was etched (Figure 5). To understand this phenomenon, sequence experiment was performed by changing the synthesis order. Thus we found that with the CuO precursor pH level around 8-9; this incident more likely was caused due to extreme alteration of pH level induced by CuO reaction. At elevated temperature, HMTA was hydrolyzed into ammonia [10-11] and lead to dissolving ZnO [12] as described in reaction (Eq. 1).

$$ZnO_{(s)} + 4NH_3 \bullet H_2O \rightarrow Zn(NH_3)_4^{2+} + 2OH^- + 3H_2O \quad (1)$$

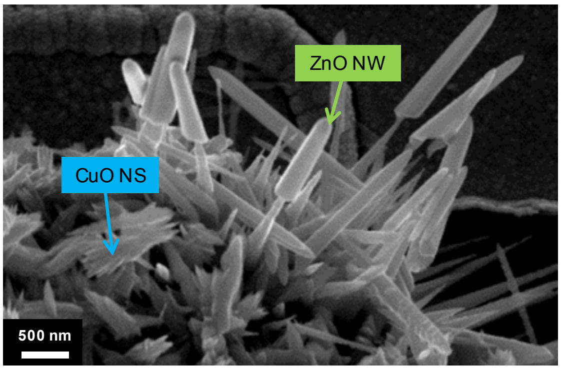

Figure 5: SEM Images of high concentration (4 mM) of CuO precursor etched ZnO NW during rapid synthesis.

We noticed that there are three important aspects to realize hybrid-nanostructures using hydrothermal method: seed layers provide sites where the nucleation starts; chemical reaction may damage base structures by changing pH level; precursor concentration and growth time are the keys for successful process.

The gas sensing performances of ZnO/CuO hybrid-nanostructures resembled as n-type semiconductor behavior since the ZnO nanowires worked as base structures. The exposure of an oxidizing gas (NO_2) led to increase the sensor resistance. Figure 7 (a) showed the sensitivity of bare ZnO NW over time at different level of temperatures (200-350 ^oC). Towards 20 ppm of NO_2 gas, bare ZnO nanowires showed responses 2134, 2561, 2957, and 3470 % when the sample was heated at 200, 250, 300, and 350 ^oC, respectively. It was observed that the response of sensor increased as the temperature was increased. The highest sensor response (S = 3470 %) was recorded at 350 ^oC. After growing CuO nanostructures using low concentration of precursor (0.25 mM), the sensor responses were changed to 1043, 7178, 1834, and 1522 % at the same level of operating temperatures.

The gas sensing mechanism of hybrid-nanostructures was based on p-n junction formation on the surface of n-type [13] or p-type [14-15] semiconductor. In bare ZnO nanowires, adsorbed oxygen species (O^-) at high temperature formed a depletion layer on the surface of nanowires. During the exposure to NO_2 gas, two possible reactions may occur at the same time. First reaction is the direct oxidation that transfers electrons from nanowires and results in negatively charged NO_2. Second reaction is the desorption reaction between the negatively charged NO_2 that was produced in first reaction with adsorbed oxygen species and this results in neutral NO_2 and O^{2-}. Both reactions are characterized by increasing resistances that means thickening of depletion layer. After growing CuO nanostructures, additional depletion layer is generated on nanowires. It was represented by increasing baseline resistance from kΩ level to MΩ level. During the exposure to NO_2 gas, both reactions constitute the change of resistances. Since the baseline resistances is shifted to higher level, the change of resistance relatively higher than its bare structures. At any rate, it only occurred at lower temperature (250 ^oC) when the maximum sensor response was obtained. Accordingly, temperature effect on CuO nanostructures might have a significant role to enhance the sensor response at lower temperature.

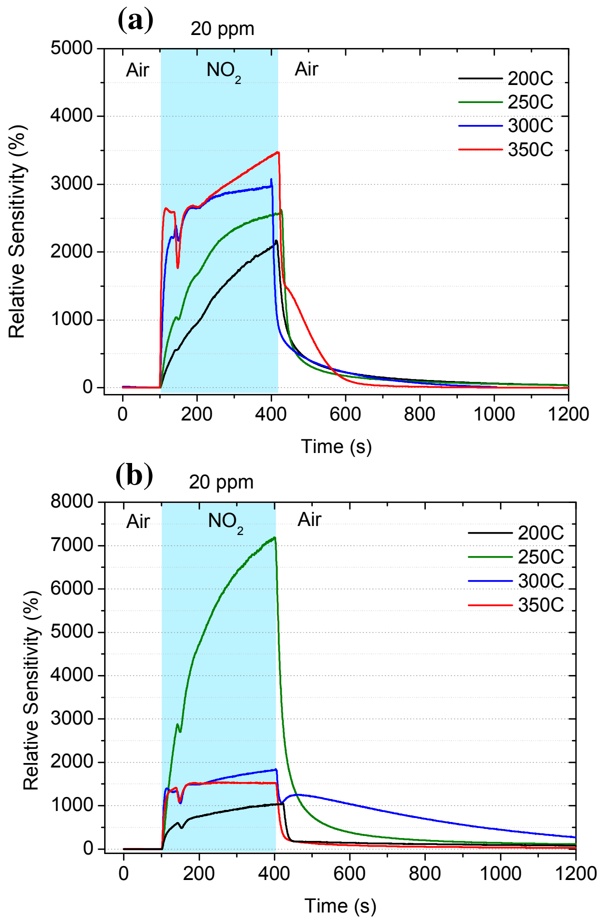

Figure 7: Gas sensing performance: (a) bare ZnO NW, and (b) ZnO NW/CuO NS at various temperatures.

CONCLUSIONS

To conclude, we demonstrated simple and fast fabrication of hybrid-nanostructures metal oxides using ZnO NW and CuO NS with enhanced sensitivity at lower operating temperature (250 ^oC). The synthesis processes were performed by hydrothermal reaction via localized Joule heating using microheaters directly on the sensing electrodes. The concentrations of CuO precursor and growth time were key factors for successful synthesis process.

ACKNOWLEDGEMENTS

This work was supported by the Center for Integrated Smart Sensors funded by the Ministry of Education, Science and Technology as Global Frontier Project (CISS-2012-M3A6A66054201) and the Future-based Technology Development Program (Nano Fields) (2012-0006203) through the National Research Foundation of Korea (NRF) funded by the Korean government (MEST).

REFERENCES

[1] G. Jime´nez-Cadena, J. Riu, and F. X. Rius, “Gas sensors based on nanostructured materials”, *Analyst*, vol. 132, pp. 1083-1099, 2007.

[2] R. S. Devan, R. A. Patil, J. Lin, and Y. Ma, “One-Dimensional Metal-Oxide Nanostructures:

Recent Developments in Synthesis, Characterization, and Applications." *Adv. Funct. Mater.*, vol. 22, pp. 3326-3370, 2012.

[3] M. E. Franke, T. J. Koplin, and U. Simon, "Metal and Metal Oxide Nanoparticles in Chemiresistors: Does the Nanoscale Matter?", *Small*, vol. 2 (1), pp. 36- 50, 2006.

[4] L. F. Zhu, J. C. She, J. Y. Luo, S. Z. Deng, J. Chen, and N. S. Xu, "Study of Physical and Chemical Processes of H_2 Sensing of Pt-Coated WO_3 Nanowire Films", *J. of Phys. Chem. C*, vol. 114, pp. 15504-15509, 2010.

[5] P. Rai, Y. Kim, H. Song, M. Song, and Y. Yu, "The role of gold catalyst on the sensing behavior of ZnO nanorods for CO and NO_2 gases", *Sens. and Actuators B*, vol. 165, pp. 133-142, 2012.

[6] A. Kolmakov, D. O. Klenov, Y. Lilach, S. Stemmer, and M. Moskovits, "Enhanced Gas Sensing by Individual SnO_2 Nanowires and Nanobelts Functionalized with Pd Catalyst Particles", *Nano Lett.*, vol. 5 (4), pp. 667-673, 2005.

[7] X. Kong and Y. Li, "High sensitivity of CuO modified SnO_2 nanoribbons to H_2S at room temperature", *Sens. and Actuators B*, vol. 105 (2), pp. 449-453, 2005.

[8] N. D. Khoang, D. D. Trung, N. V. Duy, N. D. Hoa, and N. V. Hieu, "Design of SnO_2/ZnO hierarchical nanostructures for enhanced ethanol gas-sensing performance", *Sens. and Actuators B, vol.* 174, pp. 594-601, 2010.

[9] N. Datta, N. Ramgir, M. Kaur, S. K. Ganapathi, A. K. Debnath, D. K. Aswal, and S. K. Gupta, "Selective H_2S sensing characteristics of hydrothermally grown ZnO-nanowires network tailored by ultrathin CuO layers", *Sens. and Actuators B*, 166-167, pp. 394-401, 2012.

[10] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, and X. L. He, "Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors", *Appl. Phys. Lett.*, vol. 84, pp. 3654, 2004.

[11] L. E. Greene, B. D. Yuhas, M. Law, D. Zitoun, and P. Yang, "Solution-Grown Zinc Oxide Nanowires", *Inorg. Chem.*, vol. 45(19), pp. 7535-7543, 2006.

[12] J. Zhou, N.S. Xu, and Z.L. Wang, "Dissolving Behavior and Stability of ZnO Wires in Biofluids: A Study on Biodegradability and Biocompatibility of ZnO Nanostructures", *Adv. Mater.*, vol. 18, pp. 2432–2435, 2006.

[13] H. –S. Woo, C. W. Na, I. –D. Kim, and J. –H. Lee, "Highly sensitive and selective trimethylamine sensor using one-dimensional ZnO–Cr_2O_3 hybrid-nanostructures", *Nanotechnology*, vol. 23, pp. 1-10, 2012.

[14] M. –G. Willinger, G. Neri, E. Rauwel, A. Bonavita, G. Micali, and N. Pinna, "Vanadium Oxide Sensing Layer Grown on Carbon Nanotubes by a New Atomic Layer Deposition Process", *Nano Lett.*, vol. 8 (12), pp. 4201-4204, 2008.

[15] C. Marichy, N. Donato, M. –G. Willinger, M. Latino, D. Karpinsky, S. –H. Yu, G. Neri, and N. Pinna, "Tin Dioxide Sensing Layer Grown on Tubular Nanostructures by a Non-Aqueous Atomic Layer Deposition Process", *Adv. Funct. Mater.*, vol. 21 (4), pp. 658-666, 2011.

CONTACT

*I. Park, tel: +82-42-350-3240; inkyu@kaist.ac.kr