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Analysis on Response Characteristics of Toxic Gas Sensors with ZnO Nano-Rods Structure by Heat Treatment Process

Daehwan Kwon[1], Gyoutae Park[1], Chulhee Yu[1], Youngdo Jo[1], Jongsam Moon[1], Jeungsoo Huh[2], Jun Ha[3]

[1, 2, 3, 4, 5]Institute of Gas Safety R&D Korea Gas Safety Corporation, Chung-buk, The Republic of Korea

[6]Department of Materials Science and Metallurgical Engineering, Kyungpook National University, 80 Daehakro, Bukgu, Daegu, 41566, Korea

[7]Seoin IT Ltd., Co., 45, Gasan digital 1-ro, Geumcheon-gu, Seoul, Korea

Abstract: ***Thin films of Pt and Zn were coated withon the electrode in the alumina board.Thin films of Ptare fabricatedby ion plasma and Zn ismanufactured by DC sputtering methods. Then ZnO nanostructured sensor's materials were produced on Zn film by ultrasonic process in 0.01M aqueous solution of $C_6H_{12}N_4$ and $Zn(NO_3)_2{\cdot}6H_2O$. To examine the effect of the thermal treatment for the gas response characteristics, prepared nanostructured samples were secondarily heat-treated at 400^0C for 1h in nitrogen and oxygen atmosphere respectively and sensitivity measurement test of nanostructuredand not heat-treated samplesis achieved for toxic gases.The results showed that ZnO crystallite size after annealing process was lager when using XRD. Itestimatedthat response characteristics were improved owing to lager crystallite size.The sensitivities of the secondarily heat-treated sensors are enhanced 20% in oxygen and 10% in nitrogen atmospheres.Also, better performances of repeatability and linearity appeared in the range oflow concentration than primary heat-treated.***

Keywords: Heat-treatment, ZnO, Nano-rods, Response Characteristics, Toxic gas

1. Introduction

The presence of toxic and pollution gases, such as toluene gas in the plants and at home, addition to outdoors, poses occupational and health hazards and thus gas sensing devices need to be installed in such places [1].

In the past decade, Metal-oxide gas detector have attracted substantial interest thanks to their low cost, flexible production, simple application, wide variety of detectable gases, and potential for integration with semiconductors. Various metal-oxide-based materials are used in gas detection because of their numerous advantages, such as good response characteristics [2].

The method of the semiconductor type sensor for detecting a gas by using a high temperature (200~400^{0}C) and the surface properties change due to the conductivity of the electron exchange of gas when gas is adsorbed on the surface of oxide semiconductor. ZnOSemiconductor gas sensor is a very interesting material of a 2-6 compound semiconductor having a hexagonal crystal structure called wurtzite, 3.37Ev direct transition band gap energy, and is a semiconductor having 60 meV exciton binding energy[3].

Semiconductor sensors have surface area. So as to adsorb as much of the target gas as possible on the sensor's surface, giving a stronger and more measurable response characteristics(especially at low concentrations)[4].

In this paper, we develop toxic gas sensor that can be used for toxic gas sensing device installed in wastewater treatment plant and analyze its response characteristics. In addition, this sensor suggests the possibility of being utilized for measuring toxic gas. To manufacture the toxic gas sensor, first of all, Alumina board which was coated with Pt and Zn film as the electrode and the seed layer on each side was prepared. Pt and Zn film were fabricated by ion plasma and DC sputtering methods, respectively. In addition to turn the deposited zinc powder into zinc oxide, the gas sensors were heat-treated at 600^{0}C for one hour.Then gas sensors of ZnO nanorods were manufactured by ultrasonic process in an aqueous solution of 0.01 mole.

Additional heat treatment was performed for an hour in the oxygen and nitrogen atmosphere to determine sensor's response characteristics about a secondary heat treatment effect. And sensor's response characteristics of samples were compared with as-prepared ones and original one(non-heat treatment). Through XRD analysis, we wanted to verify the crystallite size of the sensor surface. As a result, additional heat treatment has improved the crystallite size of zinc oxide. Sensor's response characteristics are compared before and after heat treatment. And Tests show that the additional heat treatment sensor has 20 % higher sensitivity to hydrogen sulfide at low concentrations. In addition, repeatability and linearity were improved by 20% and 10% respectively. Based on the results of this study, five standard toxic gas types were manufactured to measure and analyze the response characteristics in order to utilize toxic gas detection. Because sensitivity or response speed of methane gas is positive, it is also possible to develop sensors for natural gas.

2. Experimental method

As shown in Figure 1 below, the size of sensor's substrate is 4.5mm ×3.78mm×0.3t. It consists of gold electrodes and aAl_2O_3 substrate. The resistance of platinum heater (back side) is about 15. To prevent short circuits, the electrodes have positioned the holes in the semiconductor toxic gas sensors as follows:

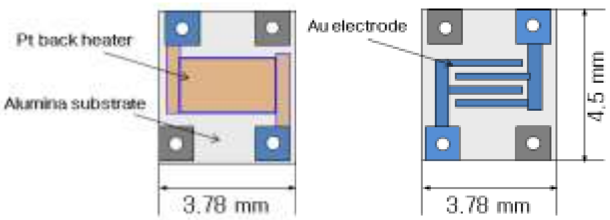

Figure 1: Offabricated sensor's substrate

In pre-treatment procedure, since it is not bonded to the zinc seed layer on the Al_2O_3 substrate. Platinum was coated by an ion coater. The thickness of Platinum was about 80Å as the bonding layer. The Zn membrane with 1000Å thickness was vacuum-metallized by the sputter machine using a metallic zinc as the seed layer. To make Zinc oxide, substrates were heat-treated at 600^0C during the 1hour by the furnace. The substrates were treated with a dissolving solution of the zinc nitrate hexhydrate[$Zn(NO_3)_2{\cdot}6H_2O$ and hexamethylenetetramine[$C_6H_{12}N_4$] in deionized water. To help the nano structures, solution is stirred for 1 hour by the stirrer. In sonication procedure, ZnOnano structures were grown by sonicator in the prepared solution. In post-treatment procedure, substrates were heat-treated at 400℃ for 1 hour in the oxygen and nitrogen atmosphere.

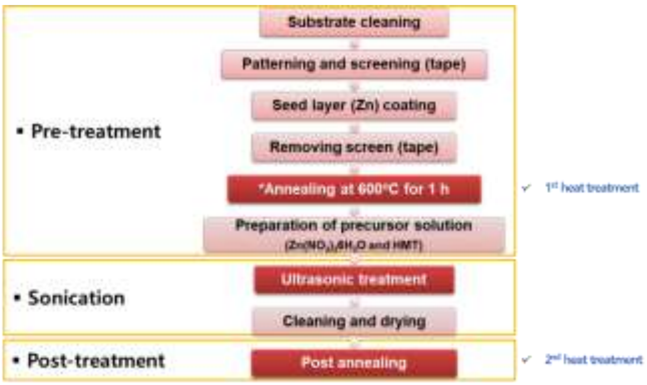

Figure 2: Total experiment process

In Figure 3, The measuring system for toxic gas detection consists of Power Supply, MFC(Mass Flow Controller), DAQ(Data Acquisition Board), the air and target gas and a circuit board. The accurate concentration control of the toxic gas was enabled using a combination of certified cylinders and a mixing system equipped with mass flow controllers and mass flow meters. A preliminary experiment to find optimum operating temperature for the gas sensing was conducted in a temperature ranges of 150 to 450^0C. And the ZnO gas sensors showed the best response characteristics at 350^0C.

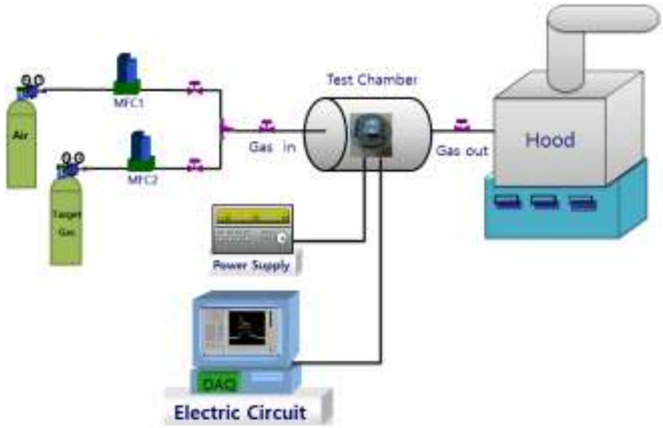

Figure 3: Response characteristics evaluation system

3. Results and Discussions

3.1 Analysis on FE-SEM of pre-treatment sensors

Figure 4 shows FE-SEM(Field Emission Scanning Electron Microscope, Hitachi SU8220) about morphologies of ZnO nanostructures. The images of U_5, U_{15}, U_{20}, U_{25} and U_{30} showed the nano particles and rods structures. Therefore, the sensors of U_{20}, U_{25} and U_{30} showed more dense nanostructures than U_5 and U_{15} sensors. It means that surface area at ZnOnanorods increased

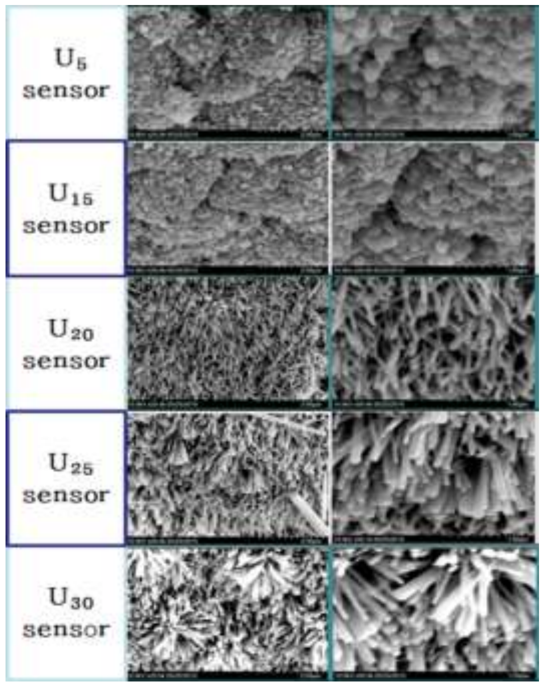

Figure 4: Analysis on FE-SEM of ZnO nanostructure

3.2 Analysis on pre-treatment of ZnO nanostructures

Figure 5 shows the sensitivity(%) and recovery(%) of ZnO nanostructure toxic gas sensors for 20ppm toluene gas. Because the sensitivity(%) of U_{30} sensor is the best value of 64%, U_{30} sensor was heat-treated to a secondary heat treatment.

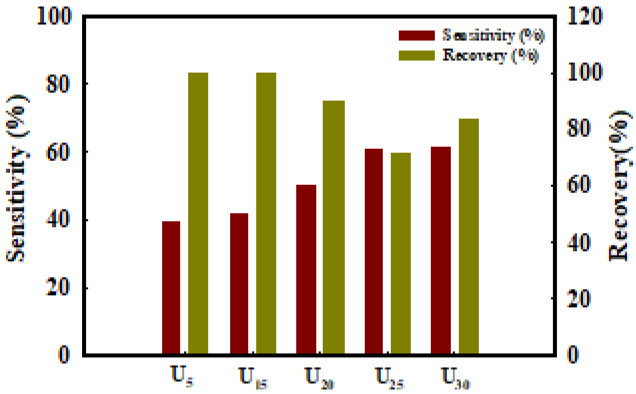

Figure 5: Sensitivity and recovery of ZnO nanostructure sensors for 20ppm Toluene gas

To verify the ZnO nanostructure of samples, Figure 6 showed X-ray diffraction(XRD, Rigaku D/Max-2500) in 2 Theta. And XRD graphs of U_{30}, U_{30_N} and U_{30_O} sensors, respectively. The peaks for (110), (101), (110), (103) and (112) direction The peak value of the secondary heat treated sensor was increased. Also crystallite size of ZnO was grown. From the XRD data, the grain sizes of ZnOnanorods were calculated and shown in Table 1. The grain size of U_{30} sensor is 190nm and that of U_{30_N} sensor is 200nm and that of U_{30_O} sensor is 208nm. Thus, the grain size was increased about 5 and 10% through heat treatment.

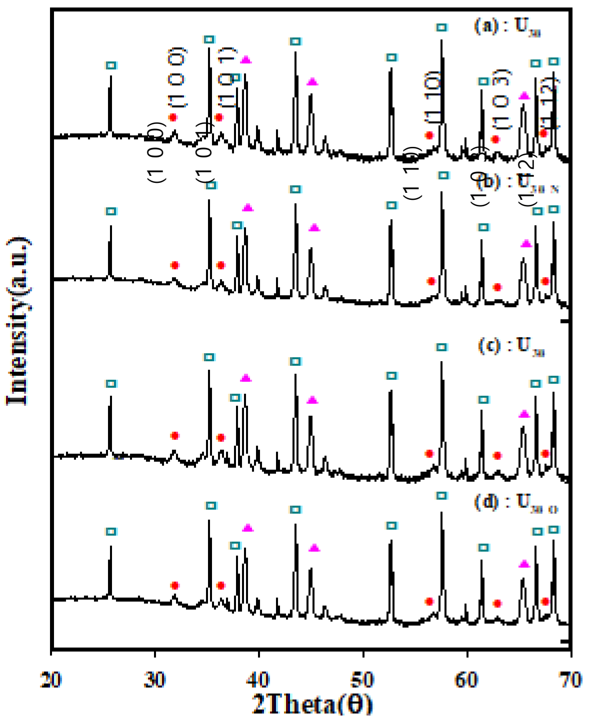

Figure 6: Comparison of XRD patterns about original and additional heat treatment sensors

Table 1: Comparison of grain size about original and additional heat treatment sensors

Sample (Sensor)	Wave length(nm)	2θ (°)	FWHM	Crystallite size(nm)
(a), (c) : U_{30}	0.154	31.8246	0.4343	190
(b) : U_{30_N}		31.8168	0.4172	200
(d) : U_{30_O}		31.8299	0.3967	208

3.3 Analysis on response characteristics of total sensors

Figure 7 shows the sensitivity and recovery characteristics of the U30, U30_N and U30_O sensors for 20ppm toluene gas. The sensitivity of the U30 sensor is 64%, and that of U30_N sensor is 70% and that of U30_O sensor is 80% which shows the enhancement of 16% between U30 and U30_O sensor.

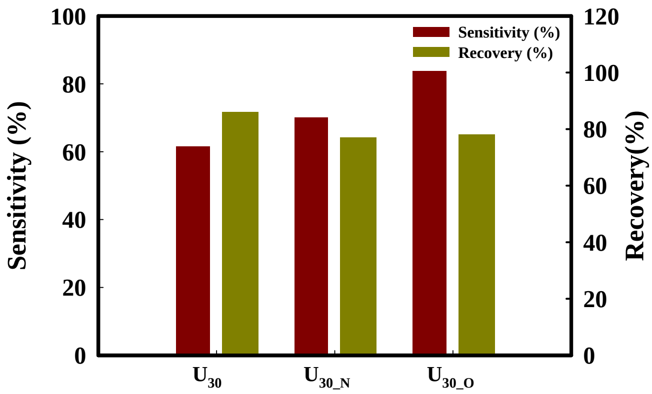

Figure 7: Sensitivity and recovery of ZnO nanostructure sensors for 20ppm Toluene gas

The reproducibility of the response characteristics of the sensors was measured in Figure 8. In this test, 20ppm of toluene gas was injected for 5 minutes and sensors were restored in the air for 15 minutes. It was repeated five times in total. During this process, three sensors showed good reproducible properties simultaneously keeping the higher sensitivity of U_{30_O} sensor.

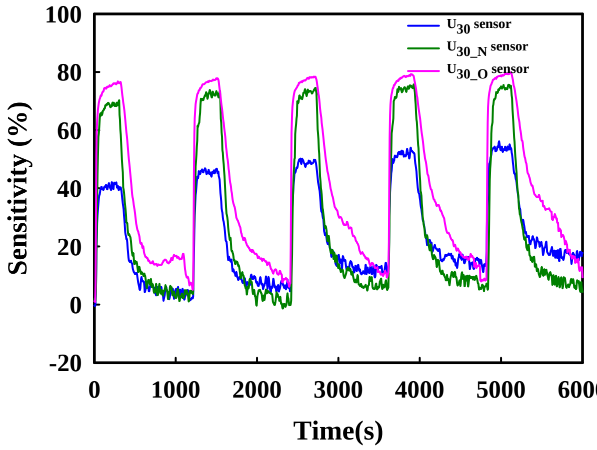

Figure 8: Reproducibility evaluation of U_{30}, U_{30_N} and U_{30_O} against toluene 20ppm

The sensing properties for various concentration of toluene were shown in Figure 9. In this experiment, a set of the toxic gas injection and the restoring process was repeated five times with changing the concentration from 1, 5, 10, 30 to 50ppm, respectively. Toluene gas was injected for 2minutes and sensors were restored for 5 minute cycle. In set shows the sensitivity change of the sensors during all experimental processes.

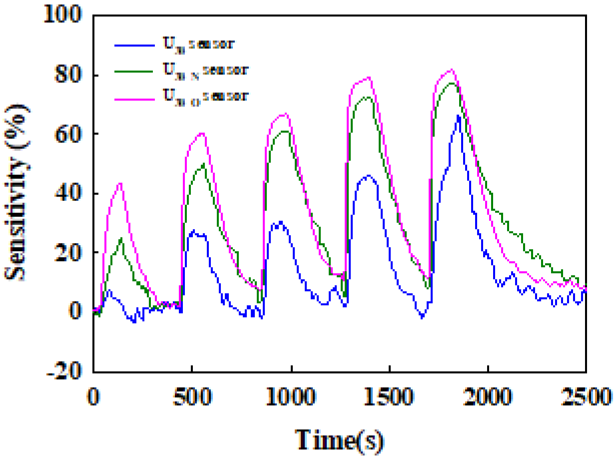

Figure 9: Response characteristics of U_{30}, U_{30_N} and U_{30_O} for toluene 1, 5, 10, 30, 50ppm

4. Conclusion

In this research, the effect of secondary heat treatment in oxygen and nitrogen atmosphere was experimented for the response characteristics of ZnO based toxic gas sensors. The results showed that ZnO crystallite size after annealing process was lager when analyzed by using XRD.Toxic gas sensors with nano-rods have good sensitivity because of the larger surface areas. It shows that sensitivity is improved in absorption and desorption response between oxygen and toxic gases.Through the secondary heat treatment, the response property of ZnO toxic gas sensor was enhanced about 20% in the response with oxygen and in the response with10% in nitrogen. Also, better performances of repeatability and linearity appeared in the range of low concentration than primary heat-treated.

5. Equations

$$S(\%) = \frac{R_{gas} - R_{air}}{R_{air}} \times 100 \quad (1)$$

$$\text{Crystallite size} = \frac{0.94(\mathit{The\ Scherrer\ Constant}\ ,\ K) \times \mathit{Wave\ Length}}{\mathit{FWHM}\,(rad) \times \cos 2\theta\,(rad)} \quad (2)$$

6. Acknowledgment

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Author Profile

Daehwan Kwon was born at Kyeong-buk Province in South Korea on Feb 7th, 1990. Now he earned the M.S. degree in School of Materials Science and Engineering at the Kyungpook University, Dae-gu, Korea in 2016. He earned B.S. degree in School of Energy System Engineering at University of Dongguk, Gyung-ju, Korea in 2014. He is currently a senior researcher of Electronic Material Engineering-based Gas Safety Facilities at Korea Gas Safety Corporation (KGS). His research interests focus metal material and gas sensors and modules.

Gyoutae Park was born at Kyeong-buk Province in South Korea on March 29th, 1970. Now he earned Ph.D degree in School of Electrical and Computer Engineering at University of Seoul, Korea in 2014. He earned the B.S. and M.S. degrees in Electronic Engineering at the Yeongnam University, Gyeongsan, Korea in 1996 and 1999, respectively. He is currently a senior researcher of Electrical and Computer Engineering-based Gas Safety Facilities at Korea Gas Safety Corporation (KGS). His research interests focus on IT convergence technology for gas safety management, gas sensors and modules, laser methane detectors, Drone gas detector, and non-dispersive infrared gas detectors. Address: 1390 Wongjung-ro, Maengdong-myon, Eumsung-gun, Chungbuk-do, 369-811, Korea.

Chulhee Yu was born at Jeon-buk Province in South Korea on August 23th, 1968. Now he earned B.S. and M.S. degree in School of Chemical Engineering at University of Jeonbuk, Korea in 1995 and 2009, respectively. He is currently a researcher of Plant based Gas Safety Facilities at Korea Gas Safety Corporation (KGS). His research interests focus on pipeline technology for gas safety management, LNG Plant, Augmented Reality, and safety scenario design. Address: 1390 Wongjung-ro, Maengdong-myon, Eumsung-gun, Chungbuk-do, 369-811, Korea

Youngdo Jo was born on July 26th, 1964. Now he earned M.S. and Ph.D degrees in School of Chemical Engineering at KAIST, Korea in 1988 and 1992, respectively. He earned B.S. degree in School of Chemical Engineering at University of Busan, Korea in 1986. He is currently a head of a Safety Research Division, Korea Gas Safety Corporation (KGS). His research interests focus on pipeline technology, high pressure and toxic gas facility, and risk assessment. Address: 1390 Wongjung-ro, Maengdong-myon, Eumsung-gun, Chungbuk-do, 369-811, Korea.

Joungsam Moon was born at Jeon-nam Province in South Korea on April 8th, 1961. Now he passed through Public administration course at Seoul National University, Korea in 2015. He passed through SPEP (SungKyunKwan Public Enterprise Program) at Sungkyunkwan University, Korea in 2005. He earned B.S. degree in School of Chemical Engineering at University of Jeonnam, Korea in 1998. He is currently a chief of Institute of Gas Safety R&D, Korea Gas Safety Corporation (KGS). He is in charging of whole research and development on gas safety.Address: 1390 Wongjung-ro, Maengdong-myon, Eumsung-gun, Chungbuk-do, 369-811, Korea.