The Effect of Calcination Temperature Variation on the Sensitivity of CO Gas Sensor from Zinc Oxide Material by Hydrothermal Process

Diah Susanti[1], Ridhwan Haliq[1], Hariyati Purwaningsih[1], Lukman Noerochiem[1] & George Endri Kusuma[2]

[1] Department of Materials and Metallurgical Engineering, Sepuluh Nopember Institute of Technology, Indonesia

[2] Department of Mechanical Engineering, Surabaya State Ship-building Polytechnic, Indonesia

Correspondence: Diah Susanti, Department of Materials and Metallurgical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, 60111, Indonesia. E-mail: santiche@mat-eng.its.ac.id

Abstract

Carbon monoxide (CO) is a poisonous gas and could be lethal towards human. A sensitive CO gas sensor is necessary to prevent accidents caused by CO gas. ZnO is a semiconductor material having many applications including gas sensors. However ZnO is rarely reported to be used as CO gas sensor material. Therefore, in this research, CO gas sensor has been prepared from ZnO material synthesized via hydrothermal process at $100°C$ for 24 hours using $ZnCl_2$ powder and NH_4OH solution. The resulted ZnO gel was subsequently dried and spin-coated on a glass substrate. The ZnO-coated glasses were then calcined at various temperatures of $500°C$, $550°C$, and $600°C$ for 30 minutes. Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) analysis were used to characterized the morphology, structure and active surface area of ZnO. The sensitivity of the ZnO material towards CO gas was measured using a potentiostat in a chamber with operating temperatures $30°C$, $50°C$, and $100°C$ with each of gas concentration 10 ppm, 100 ppm, 250 ppm, and 500 ppm. It was found that the sample calcined at $550°C$ showed the highest sensitivity towards CO gas (0.82) due to the highest active surface area ($47.2\ m^2g^{-1}$). It was also observed that the sensitivity increased with the increasing of operating temperature and CO gas concentration.

Keywords: ZnO, hydrothermal, CO gas, sensitivity

1. Introduction

CO gas is one of gases which harmful to human life. This gas is colorless, odorless and insoluble in water. It causes some poisoning symptoms such as headache, nausea, vomit, losing consciousness and even death. CO is produced from incomplete combustion processes and much discovered in the waste gas emission from motor vehicles. In the book of Environmental Health Criteria 213 about carbon monoxide published by the US environmental protection agency, it was stated that CO gas originated 50% from vehicles on the highway in a big city, 13% from non-transportation sources, 12% from combustion process in steam boilers, 8% from industrial processes, 3% from solid waste disposal and 14% from other sources (Raub, 2004)

Because of the danger of CO gas, a detector or a sensor is required as an early warning to the existence of CO gas. In our previous work (Susanti et al., 2014(a) and 2014(c)), we have used WO_3 semiconductor as a material for CO gas sensor. Besides WO_3, ZnO is also a semiconductor having many applications including gas sensors (Calestani et al., 2010, Hung, et al., 2010 and Liu, et al., 2008) and Dye Sensitized Solar Cell (DSSC) Susanti, et al., 2014(d). However, ZnO is rarely reported to be used as CO gas sensor material. ZnO is cheaper than WO_3. It has a band gap of 3.37 eV at room temperature (Tak et al., 2013), wider than WO_3 of $2.6 - 3$ eV (Gillet et al., 2004). The advantages of having a large band gap are capabilities to survive on high voltages and large electric fields and to operate at high temperature.

ZnO has been synthesized via many methods, including vapor-liquid-solid (Calestani et al., 2010), Zn sputtering and subsequent thermal oxidation of sputtered metallic Zn films in dry air (Hung et al., 2010), hydrothermal (Peng Y and Huo D., 2009), sol-gel (Tseng, et al., 2012), spray pyrolysis (Widiyastuti et al., 2012) and physical vapor deposition (PVD) (Jimenes-Cadena et al., 2010). and simple thermal oxidation of Zn powder (Khanlary et al., 2012). Each method certainly has some advantages and drawbacks. Among those mentioned methods we have successfully synthesized ZnO via hydrothermal method followed by calcination at various temperatures

500, 550 and 600°C to apply as material for DSSC (Susanti et al., 2014(d)). The resulted ZnO crystal structure was hexagonal based on XRD measurement and the morphology showed hexagonal particles based on SEM analysis. The particle and crystal sizes, along with active surface areas strongly depended on calcination temperatures. The performance of DSSC was influenced by the structure of resulted ZnO. The sample calcined at 550°C had the highest DSSC efficiency of 0.15%. The highest DSSC performance might originate from the highest active surface area of 146.2 m^{2}gram^{-1}. The more active surface area would enable the storage of more electrolyte and dye in the material, which were responsible for the conversion of light energy into electrical energy.

Hydrothermal process has been widely used to synthesize nanomaterials which results in uniform particle sizes and regular shapes, better than the resulted materials from thermo-oxidation process. Comparing with other methods such as vapor-liquid-solid, PVD and spray pyrolysis, it works at relatively low temperature because it relies on the energy generated by pressurized steam of the solvent or water in the materials placed in a sealed vessel or autoclave. Besides, hydrothermal process does not need strict controls on temperature and pressure.

Therefore, in this research, we synthesized ZnO using hydrothermal process to prepare material for CO gas sensor. The ZnO gel from hydrothermal process was spin-coated on top of glass substrate and calcined at various temperatures 500, 550 and 600°C for 30 minutes. The material was characterized by Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD) and Brunauer-Emmet-Teller analysis. The sensitivity towards CO gas was measured using potentiostat at various operating temperatures and gas concentration. The correlations between structure and CO gas sensitivity were analyzed and concluded.

2. Method

Four grams of ZnCl$_2$ (Merck) was diluted in 4 ml of 0.5 M NH$_4$OH (Merck) and 10 ml distilled water. The mixture was manually stirred well and then kept in a hydrothermal chamber in the form of 150 ml sealed Teflon-lined stainless-steel autoclave which placed inside a muffle furnace at 100°C for 24 hours. The successive reaction processes might be described as follows:

$$ZnCl_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4Cl \tag{1}$$

$$ZnCl_2 + 2NH_4OH \rightarrow ZnO + H_2O + 2NH_4Cl \tag{2}$$
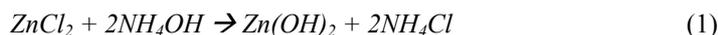
The ZnO gel from hydrothermal process was spin-coated at spinning rates of 500 rpm for 30 seconds and continued at 2000 rpm for 90 seconds on top of a 20 mm x 20 mm glass substrate and calcined at various temperatures 500°C, 550°C and 600°C for 30 minutes. The reasons behind the selection of the calcination temperatures were discussed previously in our report (Susanti, et al., 2014(d)).

XRD (Philips X-Pert XMS using X-ray Cu Kα source with wavelength of 1.54056 Å and angle range of 10-90°) and SEM (SEM FEI S-50 with a working voltage 20 kV) were utilized to characterize the structure and morphology of ZnO, respectively, before and after sensitivity test. BET measurement (Quantachrome AsiQwin using Nitrogen gas) was used to measure the active surface area of ZnO powder which was scratched from the glass substrate surface. To prepare the sensor chip, the opposite edges of glass substrate were sputtered by Pd/Au for 30 minutes to form electrodes and electrical connections.

The sensitivity test towards CO gas was performed inside a 20 liter stainless-steel chamber equipped with a thermo-controller, electrical connections to potentiostat (Versastat 4.0 by Par Ametek) instrument and channels to a vacuum pump and gas sources. The sample was placed in the middle of a ceramic disk heater inside the chamber. The chamber was initially pumped to vacuum and the sample was set at room temperature (30°C). The air was flown inside the chamber with a volume of 20 liters. The air resistance was measured using potentiostat under the potential difference of 1.5 V. The resistance of air was denoted as Ro (Ω). The CO gas was then flown inside a chamber using a mass flow controller (MFC) so that the CO concentration was set to be 10 ppm. The resistance under the presence of CO gas was measured and denoted as Rg (Ω). These steps were repetitively performed with different CO gas concentrations of 100 ppm, 250 ppm, and 500 ppm. After completion, the operating temperatures were successively changed to 50°C and 100°C, each with the same CO gas concentrations as mentioned above. The sensitivity values were calculated with the equation below (Wang et al., 2003):

$$S = |R_g - R_o| / R_o \tag{3}$$

Where S is the sensitivity of the sensor, R$_g$ is the resistance (Ω) after CO gas flowing and R$_o$ is the resistance (Ω) of air before CO gas flowing.

3. Results and discussion

Figure 1 and 2 display the SEM images of ZnO synthesized at 500°C, 550°C and 600°C before and after exposed to CO gas respectively. The two figures show some insignificant changes on the ZnO material morphologies after CO gas exposure which might be caused by mechanical treatments during sensitivity tests. The insignificant changes indicate that ZnO synthesized by hydrothermal treatment is quite stable and inert towards CO gas.

SEM images also showed that ZnO material formed rods with hexagonal shape in the top face. Some of the rods had shape like blunt pencils. The shape of hexagonal plane became more regular after calcination process at 550°C. As we have discussed in the previous report (Susanti et al., 2014(d)), according to the TGA/DSC measurement of ZnO gel after hydrothermal process, we found two exothermic peaks at 530°C and 600°C shown the beginning of ZnO crystal and phase formations. The ZnO material calcined below 550°C had polygonal shape which became more regular hexagonal shape after calcination process at temperatures higher than 550°C.

Moreover, the particles have wide ranges in sizes. For example, ZnO calcined at 500°C had rod length of ~10-15 μm and rod diameter of ~2-10 μm. ZnO calcined at 550°C had rod length ~8-12 μm and diameter of ~2-10 μm, while that calcined at 600°C had rod length ~9-11 μm and diameter of ~0.5-1 μm. ZnO calcined at 600°C was seemed to have the smallest particle sizes although the sizes of three samples were in the same order. Therefore the values of active surface area based on BET measurement (Table 1) were not quite different. From the table, the sample calcined at 550°C had the highest active surface area, followed by that calcined at 600°C and 500°C. This trend was similar to what we have reported previously in our report (Susanti, et al., 2014(d).
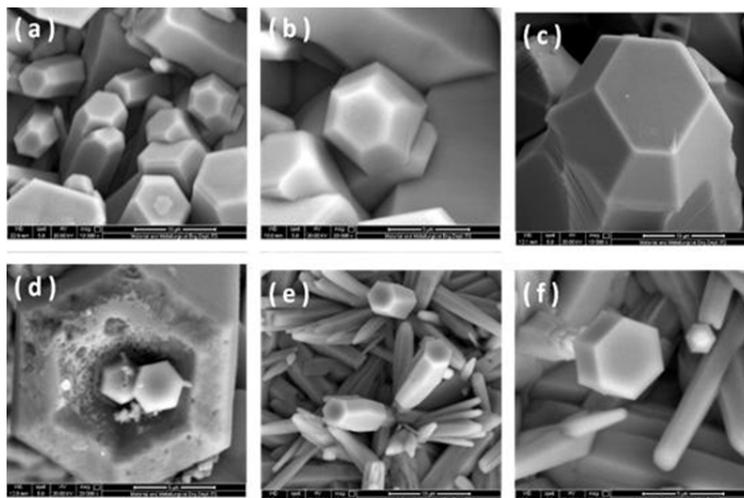
Figure 1. Bright field SEM images of ZnO material calcined at various temperatures: a) 500°C 10k x,   b) 500°C 20k x,   c) 550°C 10k x, d) 550°C 20k x, e) 600°C 10k x, dan f) 600°C 20k x before CO gas exposure at two different magnifications 10k and 20k.

Table 1. Active surface area based on BET measurement

Feature	Calcination Temperature (°C)		
	500	**550**	**600**
BET Surface area (m²g⁻¹)	39.7	47.2	44.6

Figure 3 showed the XRD patterns of ZnO samples calcined at various temperatures before and after CO gas exposure. All of the XRD patterns matched well with JCPDF card number 80-0075 of ZnO with hexagonal structure without the formation of any impurities. The XRD pattern shows the three dominant crystalline plane orientations of (100) at $2\theta = 31.76030°$, (002) at $2\theta = 34.43430°$, (200) at $2\theta = 36.25020°$. The intensities of the XRD peaks changed after CO gas exposure especially in the samples calcined at 500°C and 550°C. The changes were perhaps influenced by the variation in operating temperatures during sensitivity measurements.
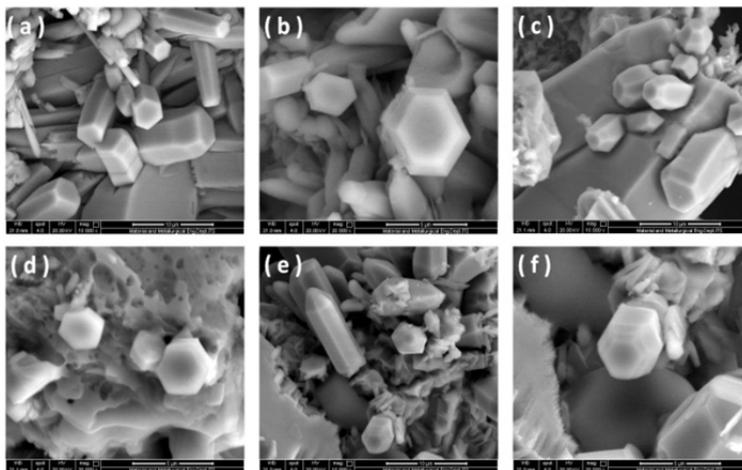
Figure 2. Bright field SEM images of ZnO material calcined at various temperatures: a) 500°C 10k x, b) 500°C 20k x, c) 550°C 10k x, d) 550°C 20k x, e) 600°C 10k x, dan f) 600°C 20k x after CO gas exposure at two different magnifications 10k and 20k.

(i)   **(ii)**
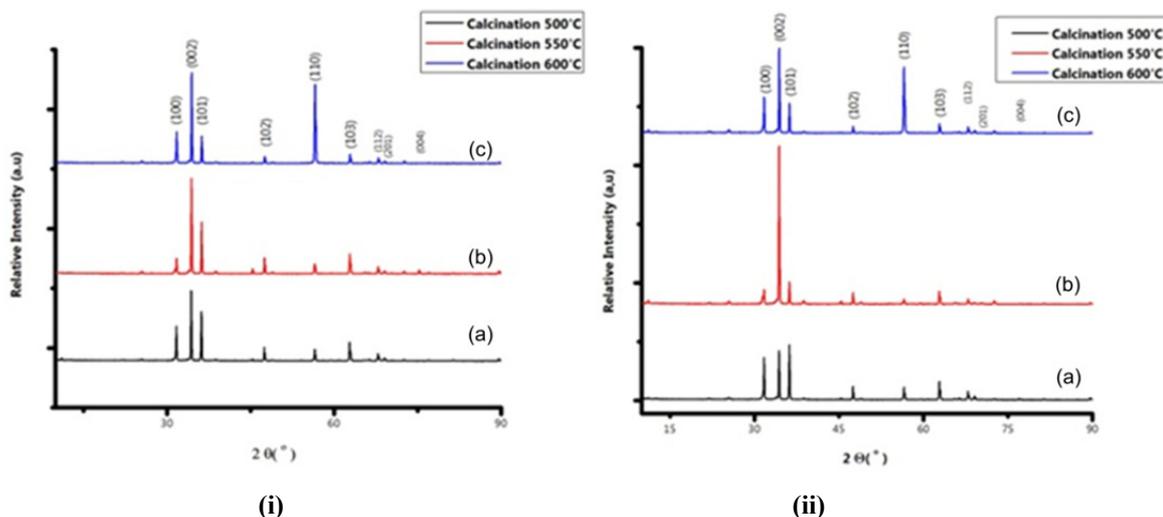
Figure 3. Comparison of the XRD measurement results of the ZnO calcined at (a) 500°C, (b) 550°C, and (c) 600°C (i) before and (ii) after exposure to CO gas

Figure 3 showed the XRD patterns of ZnO samples calcined at various temperatures before and after CO gas exposure. All of the XRD patterns matched well with JCPDF card number 80-0075 of ZnO with hexagonal structure without the formation of any impurities. The XRD pattern shows the three dominant crystalline plane orientations of (100) at $2\theta = 31.76030°$, (002) at $2\theta = 34.43430°$, (200) at $2\theta = 36.25020°$. The intensities of the XRD peaks changed after CO gas exposure especially in the samples calcined at 500°C and 550°C. The changes were perhaps influenced by the variation in operating temperatures during sensitivity measurements.

Table 2 lists the crystalline sizes (D in Å) of ZnO before and after sensitivity test towards CO gas based on Debbye-Scherrer's formula (Cullity and Stock, 2001):

$$D = \frac{0.9\,\lambda}{B\,\cos\theta} \tag{4}$$

where λ is the wavelength of X-ray source (Å), B is full-width at half maximum (radian) and θ is the angle of the highest peak (radian).

Table 2. The crystalline size of ZnO calcined at various temperatures before and after sensitivity test towards CO gas

Calcination Temperature ($^\circ$C)	D (Å) before sensitivity test	D (Å) after sensitivity test
500	1012.04	815.61
550	810.82	577.73
600	810.82	809.23

From table 2, the sample crystalline sizes changed after sensitivity test except the crystalline size of the sample calcined at 600°C. It was not CO gas which influenced the changes in the crystalline sizes, because from the XRD pattern, there was no other phase beside ZnO which could be observed. Therefore, it must be thermal and mechanical treatments during sensitivity test which affected the changes. Comparing with CO gas sensor prepared from ZnO synthesized by direct thermo oxidation from Zn powder we wrote in other paper (Susanti, et al., 2014(b)), this thin film of ZnO from hydrothermal process was less stable.

The sensitivity of the sensor is strongly affected by the operating temperatures and the concentrations of CO gas as shown in Figure 4 and 5. The sensitivity of the sensor increased with operating temperatures and CO gas concentrations. The sensing mechanism of the sensor could be expressed as below (Kocemba and Rynkowski, (2011):

$$Oxidation: \quad 1/2\ O_2^g\ +\ e^-\ \leftrightarrow\ O^{ad-} \tag{5}$$
$$Reduction: \quad CO\ +\ O^{ad-}\ \leftrightarrow\ CO_2^g\ +\ e^- \tag{6}$$
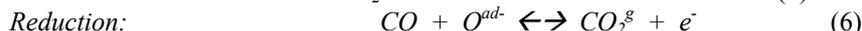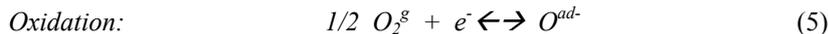
The oxygen molecules from the air would be adsorbed onto ZnO surface area and would extract the electrons from the conduction band of ZnO. The electrons from ZnO valence band would be excited to conduction band. When CO gas was present, the adsorbed oxygen and CO gas would react to form CO_2 gas. As CO gas concentration increased, there would be more oxygen molecules which reacted with CO gas. Hence more electrons would be extracted from the conduction bands and would jump from the valence band. This situation would lead to the increasing of material electrical resistance. The increasing of electrical resistance would cause the increasing in sensitivity. When O_2 molecules have reacted with CO gas to become CO_2 gas, CO_2 would be released and the electrons would be back to the conduction band of ZnO as shown in equation (5) and (6). The electron flows influence the electrical resistance changes of ZnO sensor.
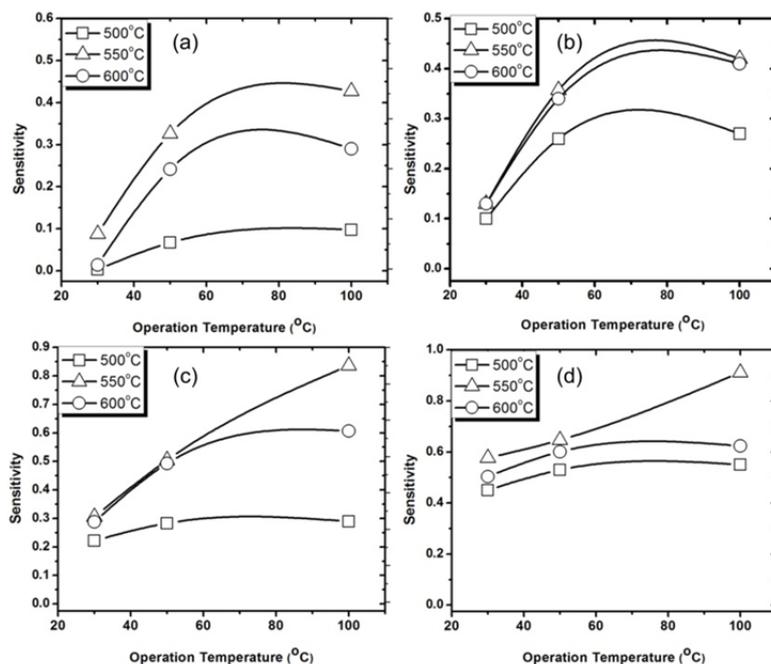
Figure 4. The sensitivity test of ZnO-based CO gas sensor calcined at various temperatures 500°C, 550°C and 600°C at different operating temperatures 30°C, 50°C and 100°C and CO gas concentration) a)10ppm, b) 100ppm, c) 250ppm, d) 500ppm

The reaction process and the jumping of electrons from valence band to conduction band would certainly require energy. Therefore the sensitivity increased with the increasing of operating temperature, since higher operating temperature gave more energy for more electrons to be bonded by oxygen molecules that reacted with CO gas, leading to the increasing of electrical resistance and sensitivity (Wang, et al., 2003).
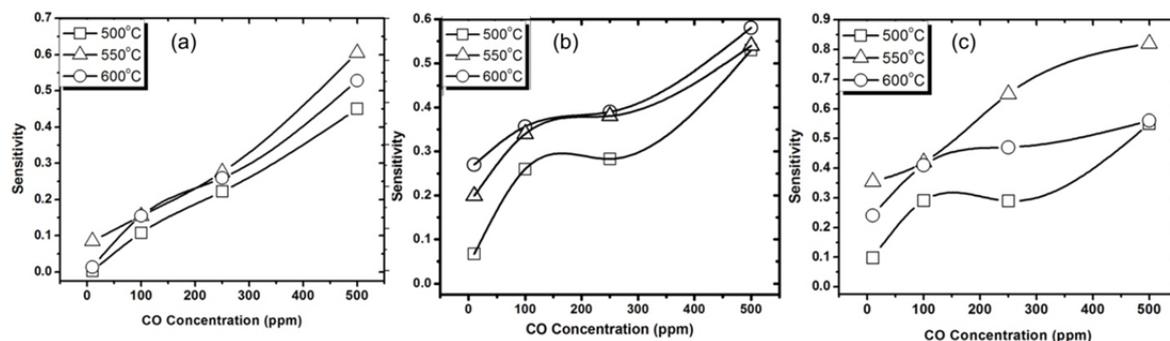
Figure 5. The sensitivity test of ZnO-based CO gas sensor calcined at various temperatures $500°C$, $550°C$ and $600°C$ at different CO gas concentration 10, 100, 250 and 500 ppm and operating temperatures a) $30°C$ b.) $50°C$ c.) $100°C$

Figure 4 and 5 showed that the sample calcined at $550°C$ had the highest sensitivity towards CO gas (0.82), followed by those calcined at $600°C$ and $500°C$. This trend was in-line with the trend of active surface area based on BET measurement (table 1), in which the sample calcined at $550°C$ had the highest active surface area, followed by those calcined at $600°C$ and $500°C$. Higher active surface area would accommodate more CO gas so that the sensitivity would be higher. Tamaki et al. (1994) also reported that the grain size strongly influenced the sensitivity of WO_3 to nitrogen oxides. The sensitivity of the sensor increased as the grain size decreased.

These results on sensitivity towards CO gas were averagely higher than our results (Susanti et al., 2014(b)) using ZnO from thermo-oxidation process. However, the structures of the ZnO material synthesized via hydrothermal process were less stable to be applied as sensor than ZnO from thermo-oxidation process. The sensitivity results towards CO gas were also lower than the sensitivity of sensor material from WO_3 that we have reported before, because the active areas of WO_3 material were higher than ZnO (Susanti et al., 2014(a) and 2014(c)). There are some aspects such as the particle size, crystallite size, active surface area, oxygen vacancy, crystallinity, material electrical conductivity and interdependency among those aspects which influence the material sensitivity. Despite of the lower sensitivity, ZnO has been proved to be a good candidate for CO gas sensor material.

4. Conclusion

CO gas sensor has been prepared from thin film of ZnO synthesized via hydrothermal process, spin-coated on top of glass substrate and followed by calcination at various temperatures 500, 550 and $650°C$. XRD measurements confirmed the formation of ZnO having hexagonal structure without any other impurities. The active surface area of sensor material strongly influenced the ZnO sensor material sensitivity towards CO gas, positioning the sample calcined at $550°C$ which had the higher active surface area to be the most sensitive sensor towards CO gas (S = 0.82 at 500 ppm CO gas concentration and $100°C$ operating temperature), followed by the samples calcined at $600°C$ and $500°C$. It was also showed that the sensitivity towards CO gas increased with operating temperature and CO gas concentration. SEM and XRD analysis have showed that there were some little morphology and structural changes of ZnO material after CO gas exposure. Despite of the small changes after CO gas exposure, this work has revealed the potency of ZnO as a good candidate for CO gas sensor material.

References

Calestani, D., Zha, M., Mosca, R., Zappettin, A. I., Carotta, M. C., Natale, D. V., & Zanotti, L. (2010). Growth of ZnO tetrapods for nanostructure-based gas sensors. *Sensors and Actuators B: Chemical, 144*(2), 472–

478.

Cullity, B. D., & Stock, S. R. (2001). *Elements of X-Ray Diffraction* (3rd ed.). New Jersey, USA: Prentice Hall, pp. 170.

Gillet, M., Mašek, K., & Gillet, E. (2004). Structure of tungsten oxide nanoclusters. *Surface science, 566*, 383-389.

Hung, N. L., Ahn, E. S., Jung, H. C., Kim, H. J., & Kim, D. J. (2010). Synthesis and Gas Sensing Properties of ZnO Nanostructures. *Journal of the Korean Physical Society, 57*, 1784-1788.

Khanlary, M. R., Vahedi, V., & Reyhani, A. (2012). Synthesis and characterization of ZnO nanowires by thermal oxidation of Zn thin films at various temperatures. *Molecules, 17*(5), 5021-5029.

Kocemba, I., & Rynkowski, J. (2011). The influence of catalytic activity on the response of Pt/SnO_2 gas sensors to carbon monoxide and hydrogen. *Sensors and Actuators B: Chemical, 155*(2), 659-666.

Liu, C. Y., Chen, C. F., & Leu, J. P. (2008). Fabrication and CO sensing properties of mesostructured ZnO gas sensors. *Journal of The Electrochemical Society, 156*(1), J16-J19.

Peng, Y., & Huo, D. (2009). Hydrothermally Grown ZnO Crystal. *Proceeding of International Symposium on Chemical Engineering of New Materials (ISCENM) 2009*, Harbin, People Republic China (PRC), pp. 694-699.

Raub, J. (2004). *Environmental Health Criteria 213: Carbon Monoxide.* US Environmental protection agency. North Carolina, USA. Retrieved from http://www.inchem.org/documents/ehc/ehc/ehc213.htm

Susanti, D., Lutfiana, E., Nurdiansah, H., Purwaningsih, H., Noerochim, L., & Kusuma, G. E. (2014b). *Preparation of CO gas sensor from ZnO Material Synthesized via Thermo-Oxidation Process,* Paper presented at the 2nd International Seminar on Fundamental and Application of Chemical Engineering 2014 (ISFAChE 2014), Kuta-Bali, Indonesia.

Susanti, D., Diputra, A. A. G. P., Tananta, L., Purwaningsih, H., Kusuma, G. E., Wang, C. H, Shih, S. J., & Huang, Y. S. (2014a). WO_3 nanomaterials synthesized via a sol-gel method and calcination for use as a CO gas sensor. *Frontiers of Chemical Science and Engineering, 8*(2), 179-187.

Susanti, D., Perdana, A. S., Purwaningsih, H., Noerochim, L., & Kusuma, G. E. (2014c). Preparation of CO Gas Sensor from WO_3 Nanomaterial Synthesized via Sol-Gel Method Followed by Hydrothermal Process, *AIP Conference Proceedings, 1586*, 14-19.

Susanti, D., Prasatya, A. N., Purwaningsih, H., Fajarin, R., & Rohmanuddin T. N. (2014d). Dye Sensitized Solar Cell (DSSC) Based on ZnO and Tamarillo Extract, *in Proceedings of the 3rd Applied Science for Technology Application (ASTECHNOVA 2014)*. International Energy Conference, Yogyakarta, Indonesia.

Tak, S. K., Shekhwat, M. S., & Mangal, R. (2013). Electrical Property of Conventionally Sintered ZnO, *International Journal of Modern Physics: Conference Series, 22*, 501–510.

Tamaki, J., Zhang, Z., Fujimori, K., Akiyama, M., Harada, T., Miura, N., & Yamazoe, N. (1994), Grain-size effects in tungsten oxide-based sensor for nitrogen oxides, *Journal of Electrochemical Society, 141*, 2207–2210.

Wang, S. H, Chou, T. C., & Liu, C. C. (2003). Nano-crystalline tungsten oxide NO_2 sensor. *Sensors and Actuators B: Chemical, 94*(3), 343–351.

Copyrights