Ethanol Sensing Properties of Zinc Oxide Nanobelts Prepared by RF Sputtering

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ABSTRACT

ZnO nanobelts were prepared on copper tube by radio frequency (RF) sputtering. From Field Emission Scanning Electron Micrograph (FE-SEM), the size of ZnO nanobelts ranged from 10–100 nm. The ethanol sensing properties of ZnO nanobelts were observed from the resistance change under ethanol vapor atmosphere at ethanol concentrations of 50, 500 and 1000 ppm and at temperature of 200–290°C. It was found that the sensitivity and response time of ZnO nanobelt sensor depended on ethanol concentration and temperature. The sensor exhibited high sensitivity and fast response to ethanol vapor at a work temperature of 220°C. These results suggested that ZnO nanobelts could have a potential application as an ethanol nano gas sensor.

Key words: ZnO, nanobelts, RF sputtering, Ethanol sensing

INTRODUCTION

One of the novel properties of semiconducting nanostructures is having a very large surface-to-volume ratio. Since the gas-sensing properties strongly depend on a surface of the materials, the gas sensors based on nanostructures of semiconducting metal oxide are expected to exhibit better sensing properties than bulk or thin film sensors.

ZnO is one of the promising semiconducting metal oxides for gas sensor applications. ZnO ceramic and thin film gas sensors were widely investigated (Cheng et al., 2004; Shishiyanu et al., 2005). Recently, gas sensors of ZnO nanostructures have caught great attention. Wan and coworkers studied gas sensor based on ZnO nanowires prepared by thermal evaporation and fabricated with microelectromechanical system (MEMS) technology. They found that the sensor exhibited high sensitivity and fast response time to ethanol gas at a work temperature of 300°C (Wan et al., 2004). Xue and coworkers studied gas sensors fabricated from $ZnSnO_3$ nanowires and found that they exhibited a very high sensitivity to ethanol gas and up to about 42 against 500 ppm ethanol gas at the operating temperature of 300°C. Both the response and recovery time were about 1 s (Xue et al., 2005). However, ZnO is also sensitive with other gasses as indicated by a few reports of ZnO nanorods sensing with hydrogen-selective. Wang and coworkers studied a sensor of ZnO nanorods synthesized by sputter-deposition. The results showed sensitivity, response and recovery time of ZnO nanorods to hydrogen concentration in N2 of 10-500 ppm and working at room temperature (Wang et al., 2005).

ZnO nanostructures can be synthesized by various growth techniques such as pulsed laser deposition (PLD) (Choopun et al., 2005(b)), chemical vapor deposition (CVD) (Hirate et al., 2005), thermal evaporation (Liu et al., 2005) and sputtering technique (Choopun et al., 2005(a)). From our previous report, we could synthesized ZnO nanobelts on copper substrate by rf sputtering.

In this work, gas sensors based on ZnO nanobelts were fabricated and we report on the ethanol sensing properties of the sensors at various ethanol concentrations and work temperatures.

MATERIALS AND METHODS

The ZnO nanobelts were synthesized on copper tube substrate by radio frequency sputtering at argon pressure of 40 mtorr, power of 300 W and duration time of 60 min. The general morphology of products on copper tube was characterized, using the field emission scanning electron microscope (FE-SEM). The gas sensors based on ZnO nanobelts were fabricated with Ag electrodes at each end of the tube with a coil heater inserted into the tube. The gas sensor was put in cylindrical gas flow chamber with 10 cm in diameter, 15 cm in height. The characteristics of sensor were measured by changing of resistance in air and in ethanol ambient with ethanol concentration of 50, 500 and 1,000 ppm and at work temperature of 200–290°C. The response and recovery were monitored and recorded via interfaced personal computer.

RESULTS AND DISCUSSION

ZnO nanobelts sputtered on the copper tube appeared white, indicating nanostructures. The general morphology of the obtained ZnO nanobelts by FE-SEM is shown in Figure 1 (a) and (b) at magnification of 2,500 and 25,000, respectively. ZnO nanobelts with ranging size of 10–100 nm and the length of around several micrometers were observed.

The response and recovery curves of gas sensors based on ZnO nanobelts upon exposure to ethanol concentration of 50, 500, and 1,000 ppm at a work temperature of 220°C are shown in Figure 2 (a). At the beginning, when there was no ethanol gas flow in the chamber, the measured resistance was steady. But after injection and removal of ethanol gas from the ambient, the resistance changed rapidly and the magnitude of the resistance change depended on the ethanol concentration. Figure 2 (b) shows the response and recovery curves at ethanol concentration of 50 ppm at various work temperatures of 200–290°C. Clearly, the characteristics of sensor depend on the work temperatures. Since the ZnO nanobelts are semiconducting material, the electron concentration in conduction band depends on temperature. At high work temperature of 290°C, the resistance of ZnO nanobelts is at the lowest value.

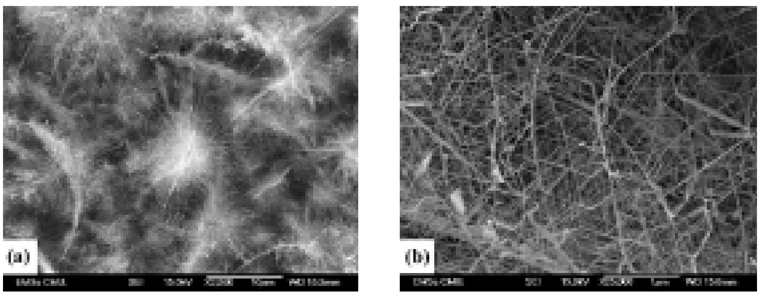

Figure 1. Morphology of ZnO nanobelts on copper tube substrate by FE-SEM with magnification of (a) 2,500 and (b) 25,000.

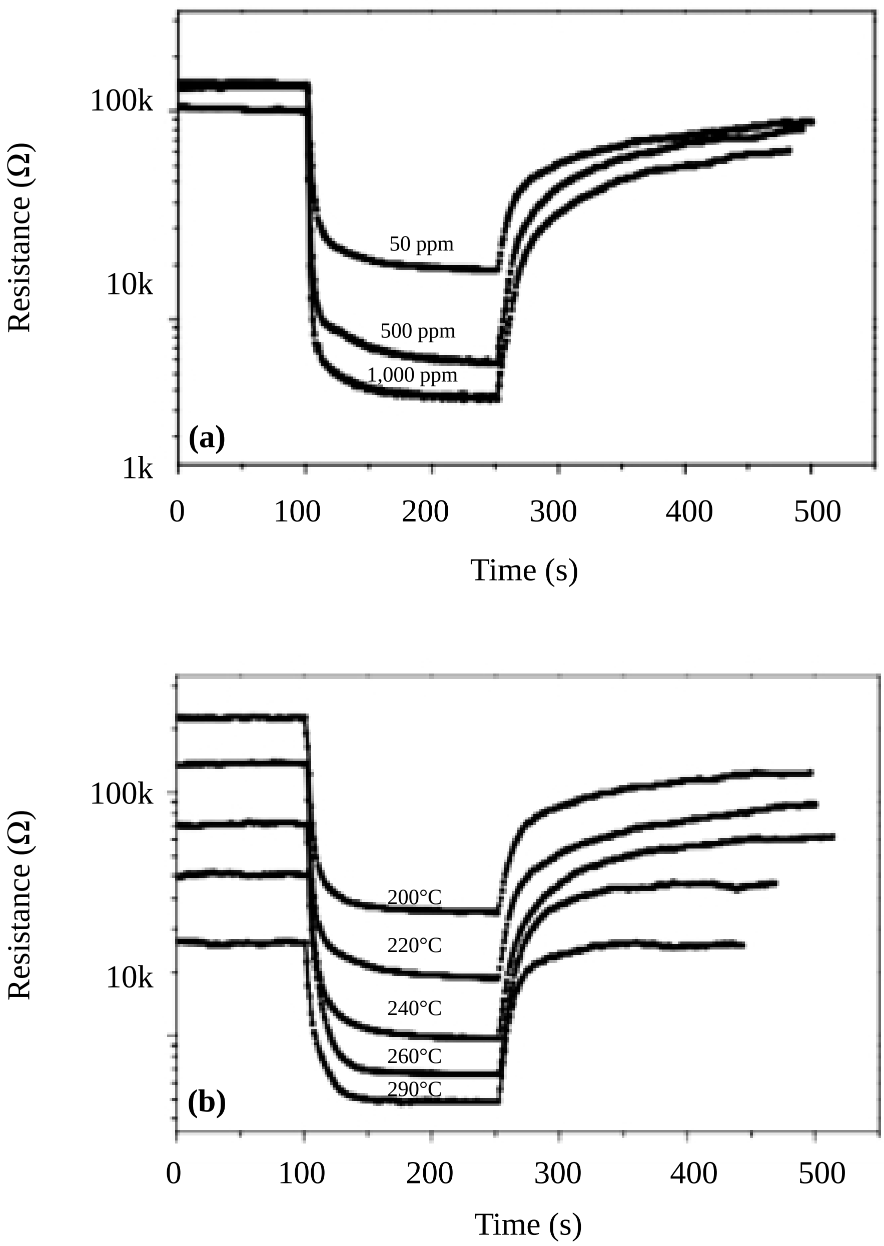

Figure 2. (a) Response and recovery characteristics of ZnO nanobelts upon exposure to ethanol with concentration of 50, 500, and 1,000 ppm at 220°C and (b) with a concentration of 50 ppm at 200–290°C.

The typical parameters to characterize gas sensor are sensitivity and response time which can be obtained from response and recovery curves. The sensitivity, S_g, of the sensor is defined as R_a / R_g and $\Delta R / R_a$, respectively, where R_a is the electrical resistance of sensor in air, and R_g is the electrical resistance of sensor in ethanol-air mixed gas. The obtained sensitivity of ZnO nanobelt sensor as a function of concentration and work temperature is plotted in Figure 3 (a) and (b).

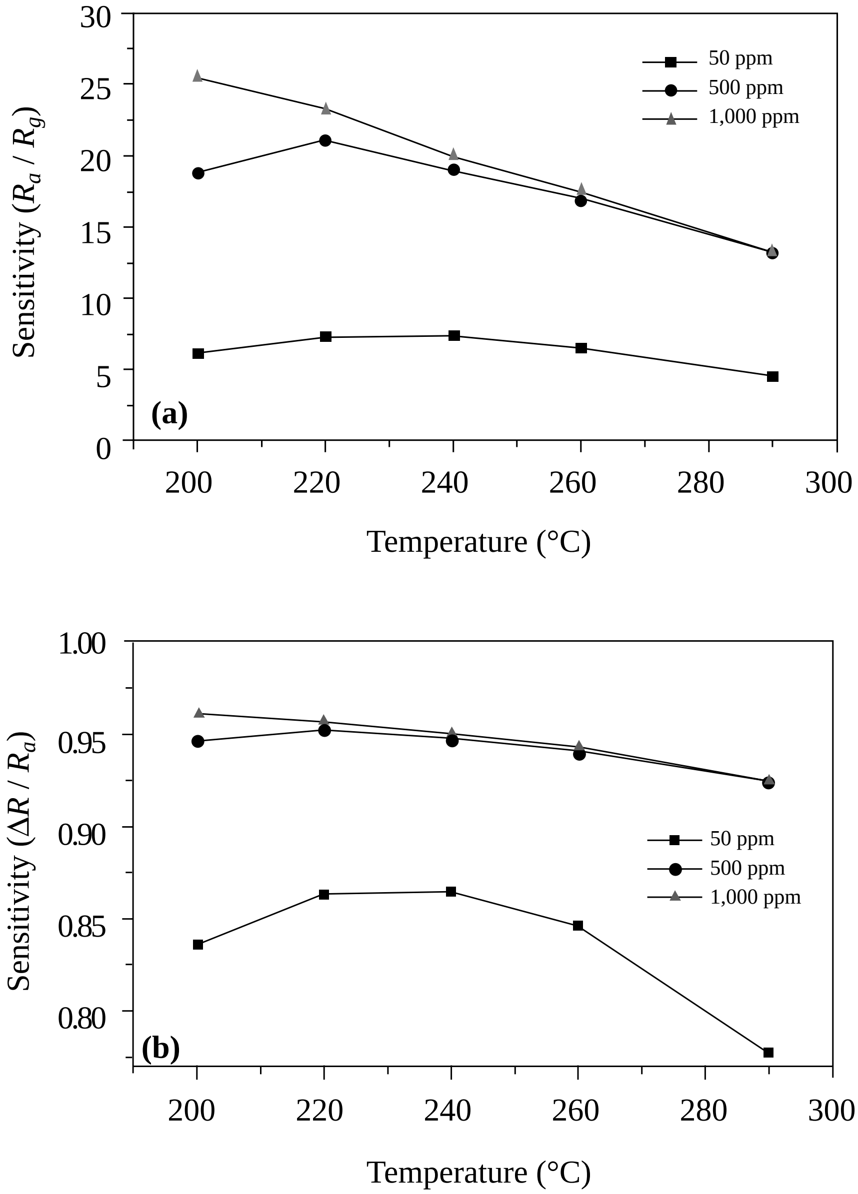

Figure 3. Plot of sensitivity which is defined as (a) R_a / R_g and (b) ΔR / R_a as a function of ethanol concentration and work temperature.

The sensitivity depends on ethanol concentration at each work temperature. The sensitivity increases with increasing the ethanol gas concentration. For example, at 50 ppm is 7.3 and at 1,000 ppm is up to 23.2. For comparison, the sensitivity of ZnO nanowires with MEMS sensor was reported to be 15 with 50 ppm ethanol at work temperature of 300°C (Wan et al., 2004), and the sensitivity of ZnO ceramic gas sensor was reported to be less than 2 with 200 ppm at 300°C (Rao, 2000). The sensitivity of our sensor is still not high and it is an on-going research to enhance the sensitivity. Moreover, the sensitivity also depends on the work temperature at each ethanol concentration. The optimized work temperature is about 220°C.

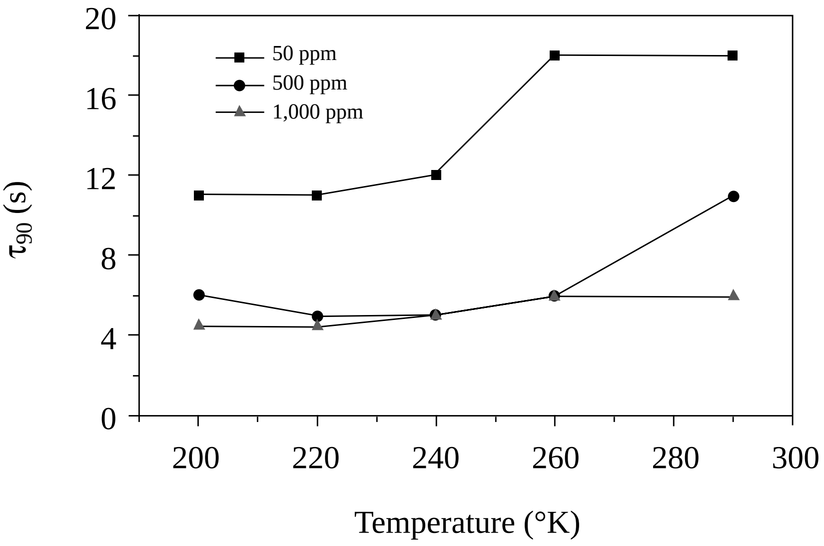

Figure 4. Plot of response time, τ_{90}, of ZnO nanobelts ethanol gas sensor with 50, 500, and 1,000 ppm of ethanol concentration and at 200–290°C of work temperature.

The response time , τ_{90}, of sensor is defined as $t_s - t_{90}$ where t_s is a starting time of flowing ethanol gas into chamber and is a time at the resistance of sensor decrease to 90 percent of $R_a - R_g$. The response time as a function of ethanol concentration and work temperature is plotted in Figure 4. The response time decreases with increasing the ethanol gas concentration and increases as work temperature increases. For example, at 500 ppm and at temperature of 200°C, τ_{90} is 6 s and is up to 10 s at temperature of 290°C.

It had been reported that the gas sensing mechanism of most oxide semiconductor gas sensors was based on the absorption of gas on the surface (Wan et al., 2004). So we believe that the same mechanism has occurred in our ZnO nanobelts gas sensor. When ZnO nanobelts gas sensor is exposed to air, an oxygen ion molecular is absorbed onto the surface of ZnO nanobelts sensor to form O_2^- ion by attracting an electron from conduction band of the ZnO nanobelts as shown in equation $O_2 + 2e \rightarrow O_2^{2-}$ or $2O_2 + 1e \rightarrow 2O_2^-$. So the high resistance of ZnO nanobelts is present in air. For active ethanol gas at moderate temperature, the ethanol gas reacts with oxygen ion molecular on the surface and gives up electron as can be described by:

$$2C_2H_5OH+O_2^{2-} \rightarrow 2CH_3CHO+2H_2O+2e$$
$$2C_2H_5OH+O_2^{-} \rightarrow 2CH_3CHO+2H_2O+1e.$$

Thus, the electrons released from the surface reaction transfer back into the conduction band which increase the conductivity and lower resistance of ZnO nanobelts.

CONCLUSION

In conclusion, ZnO nanobelts on copper tube substrate were prepared and the gas sensors based on ZnO nanobelts were fabricated. The ethanol sensing properties of ZnO nanobelts were observed from the resistance change under ethanol vapor atmosphere at ethanol concentration of 50, 500 and 1,000 ppm and at temperature of 200–290°C. It was found that the sensitivity and response time of ZnO nanobelt sensor depended on ethanol concentration and temperature. The sensor exhibited high sensitivity and fast response to ethanol vapor at a work temperature of 220°C. These results suggest that ZnO nanobelts have a potential application as an ethanol nano gas sensor.

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REFERENCES

Cheng, X. L., H. Zhao, L. H. Huo, S. Gao, and J. G. Zhao. 2004. ZnO nanoparticulate thin film: preparation, characterization and gas-sensing property. Sens. Actuators B. 102 : 248–252.

Choopun, S., N. Hongsith, S. Tanunchai, T. Chairuangsri, C. Krua-in, S. Singkarat, T. Vilaithong, P. Mangkorntong, and N. Mangkorntong. 2005(a). Single-crystalline ZnO nanobelts by rf sputtering. J.Cryst.Growth. 282 : 365–369.

Choopun, S., H. Tabata, and T. Kawai. 2005(b). Self-assembly ZnO nanorods by pulsed laser deposition under argon atmosphere. J. Cryst. Growth. 274 : 167–172.

Hirate, T., S. Sasaki, W. Li, H. Miyashita, T. Kimpara, and T. Satoh. 2005. Effects of laser-ablated impurity on aligned ZnO nanorods grown by chemical vapor deposition. Thin Solid Films (in press).

Liu, D. H., L. Liao, J. C. Li, H. X. Guo, and Q. Fu. 2005. Preparation and photo luminescence of ZnO nanostructures by thermal evaporation growth without catalysts. Mater. Sci. Eng. B. 121 : 77–80.

Rao, B. B. 2000. Zinc oxide ceramic semi-conductor gas sensor for ethanol vapour. Matts. Chem. Phys. 64 : 62–65.

Shishiyanu, S. T., T. S. Shishiyanu, and O. I. Lupan. 2005. Sensing characteristics of tin-doped ZnO thin films as NO_2 gas sensor. Sens. Actuators B. 107 : 379–386.

Wan, Q., H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin. 2004. Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. Appl. Phys. Lett. 84 : 3654–3656.

Wang, H. T., B. S. Kang, F. Ren, L. C. Tien, P. W. Sadik, D. P. Norton, S. J. Pearton, and J. Lin. 2005. Hydrogen-selective sensing at room temperature with ZnO nanorods. Appl. Phys. Lett. 86 : 243503.

Xue, X. Y., Y. J. Chen, Y. G. Wang, and T. H. Wang. 2005. Synthesis and ethanol sensing properties of $ZnSnO_3$ nanowires. Appl. Phys. Lett. 86 : 233101.

Yao, B. D., Y. F. Chan, and N. Wang. 2002. Formation of ZnO nanostructures by simple way of thermal evaporation. Appl. Phys. Lett. 81 : 757–759.