J. of the Korean Sensors Society
Vol. 17, No. 4 (2008) pp. 303 - 307

Low temperature-operating NiO-CoO butane gas sensors

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Abstract

NiO, Cu_2O, Mn_2O_3 and Cr_2O_3 as p-type semiconductors were added in CoO with 15 wt.% ethylene glycol binder and measured the butane gas sensing characteristics. The highest sensitivity is obtained for the NiO-CoO sensors. CoO-20 at.% NiO sensor with 15 wt.% ethylene glycol binder sintered at 1100 °C for 24 h exhibits high sensitivity of 90 % to 5000 ppm butane gas at the sensor temperature of 250 °C, compared to low sensitivities at the low operating temperature for commercial sensors. Response and recovery times are, respectively, within few seconds and 1min in the static flow system, indicating rapid adsorption and desorption of butane gas on sensor surface even at this low temperature.

Key Words : butane sensors, NiO-CoO, low temperature-operating, solid solution

1. Introduction

Semiconductor gas sensors have such advantages as high sensitivity, low cost, long-term stability. However, most of such sensors must operate at 300~400 °C[1-3]. Co_3O_4 ceramics may be a promising material[4] for low temperature-operating butane gas sensors because they are the most active catalyst for the oxidation of methane that is chemically the most stable among various hydrocarbon gases. Chung and Choi[5] previously experimented butane gas sensing characteristics by using Co_3O_4 sensors. Choi and Min[6] have found that Co_3O_4-NiO sensor exhibits excellent repeatability on consecutive measurements as well as long-term stability.

In this study, we attempt CoO-NiO ceramics with solid solution phase for low temperature- operating butane gas sensing. CoO phase is unstable at low temperatures in air because it changes into Co_3O_4 phase below about 900 °C. However, CoO solution phase formed by the addition of a second oxide is stable even at low temperatures. M(=Cr, Mn, Cu, Ni)-loaded CoO ceramics were tried to develop highly sensitive butane gas sensors at low temperatures.

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(Received : March 5, 2008, Revised : June 9, 2008, Accepted : June 16, 2008)

2. Experiment

20 at.% (atomic percentage) M loaded-CoO powders were prepared by wet chemical method. The starting materials of $Co(NO_3)_2 \cdot 6H_2O$ and $M(NO_3)_2 \cdot 6H_2O$ were dissolved at the molar percentage in water. The hydroxide powders were precipitated by adding 28 % NH_4OH solution at pH 9. The powders were dried at 110 °C for 24 h and fired in the temperature range 700~1100 °C for 24 h, subsequently ball-milled for 24 h to provide the starting powders for the fabrication of thick film butane sensors. The particle size of the CoO-20 at.% NiO powder sintered at 1100 °C for 24 h is 503.7 Å which is calculated from Sherrer's equation[7] by using XRD patterns. The patterns also show that NiO is solid-solutionized in CoO above 1000 °C. The stating powder mixed with various binders is screen-printed on alumina sheet and dried at 110 °C for 24 h to form thick film of 50 μm thickness. SEM view of cross-section of NiO-CoO film is shown in Fig. 1.

All the sensitivity measurements were performed to 5000 ppm i-butane gas from 150 °C to 300 °C in a static system. The sensors exhibited too low sensitivities as well as high resistance below 200 °C. The sensors, before testing the sensing characteristics, were stabilized at the operating temperature for 3~4 days. The sensitivity, S[8], is expressed in terms of sensor resistance in air (R_{air}) and in test gas (R_{gas}) as follows:

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

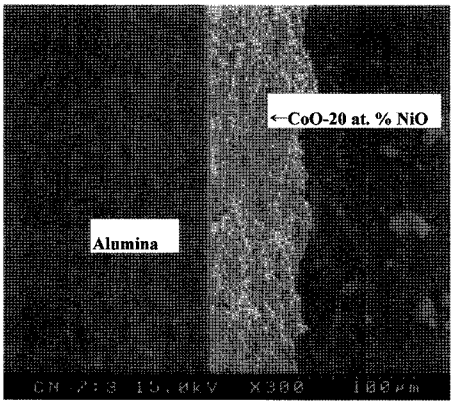


Fig. 1. Cross-section of CoO-NiO solid solution thick film on the alumina plate.

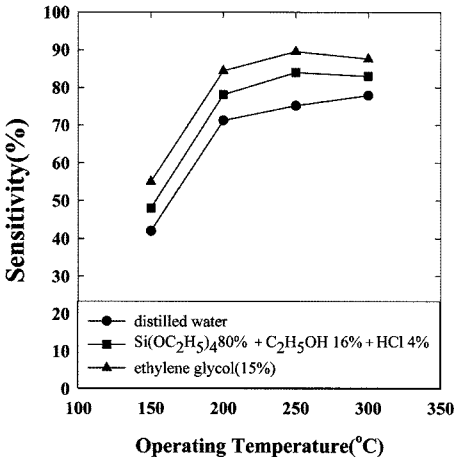


Fig. 2. Effect of various binders on the sensitivity of CoO-20 at.% NiO sensor.

3. Results and Discussion

Effect of binders such as distilled water, 80 % $Si(OC_2H_5)_4$ + 16 % C_2H_5OH + 4 % HCl (SEH) and 15 % ethylene glycol on sensitivity to 5000 ppm butane gas was investigated in terms of operating temperature. Distilled water and SEH binders provide poor adhesion of M-CoO to alumina sheet. The addition of 15 wt.% ethylene glycol to the 20 at.% NiO-CoO powders gives the best sensing characteristics as well as uniform sensitive film, as shown in Fig. 2.

Evaporation of the ethylene glycol as binder leads to more porous film that provides more contact area for the i-butane gas, resulting in very good sensitivity to the gas. Similar results were obtained in elsewhere[5].

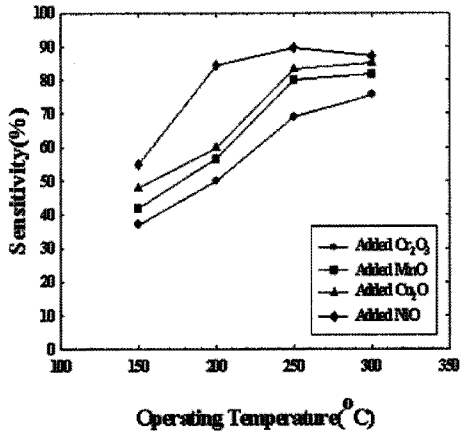


Fig. 3. Butane gas sensing characteristics of MxOy(M= Cr, Mn, Cu, Ni)-CoO sensors in terms of operating temperature.

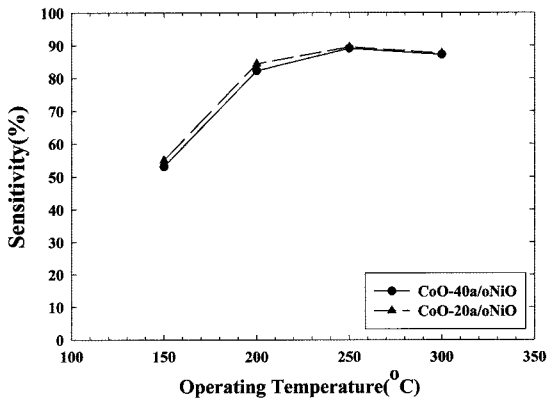


Fig. 4. Effect of NiO contents on sensitivity of CoO-NiO sensor with 15 wt.% ethylene glycol sintered at 1100 °C for 24 h.

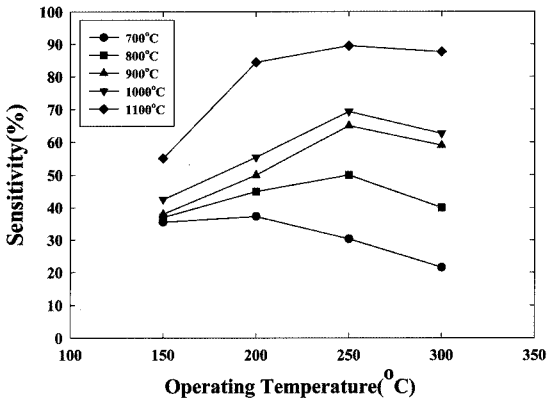
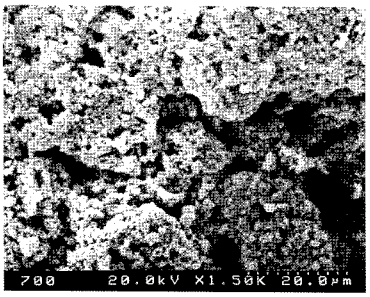


Fig. 5. Effect of sintering temperature on sensitivity of CoO-20 at.% NiO sensor.

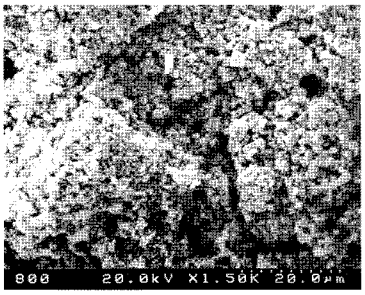
Cu_2O, NiO, Mn_2O_3 and Cr_2O_3 as p-type semiconductors were added in CoO with 15 % ethylene glycol binder and measured the butane sensing characteristics. The highest sensitivity of the NiO-CoO sensors might be due to the excellent catalytic activity of NiO in the oxidation of a hydrocarbon gas[9]. The sensitivity to 5000 ppm butane gas increases from 70 % to 90 % at 250 °C in the order of Cr-, Mn-, Cu-, and Ni loaded-CoO sensors, as in Fig. 3.

Variations of NiO content with the sensor sensitivity are investigated for the sensors sintered at 1100 °C for 24 h and at an operating temperature of 250 °C. NiO contents in CoO-NiO solid solution are in the range of 20 to 60 at.%. However, 60 at. % NiO sensor materials can hardly adhere to alumina plate, giving irregular sensing characteristic with less than 10 % sensitivity. Fig. 4 shows relationship between gas sensitivity and sensor temperature for CoO- 20 and 40 at.% NiO sensors. CoO- 20 at.% NiO sensor exhibits higher sensitivity of 90 % to 5000 ppm butane gas at the sensor temperature of 250 °C, compared to low sensitivities at the low operating temperature for commercial sensors[10].

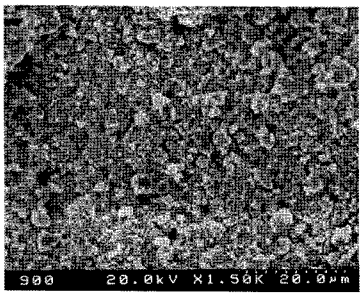
Crystallite size[9] and porosity of sensor materials are significantly affected by variations in sintering temperature and time[10], indicating strong dependence on sen-



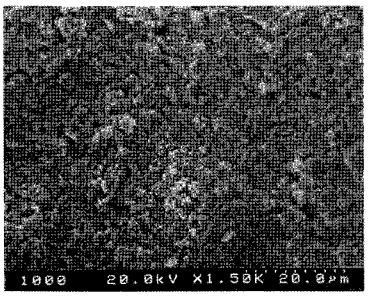
(a) 700℃



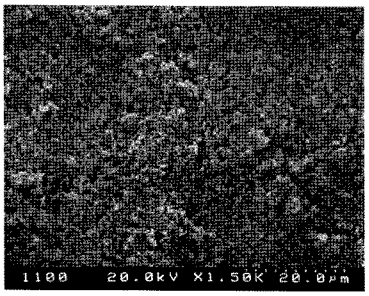
(b) 800℃



(c) 900℃



(d) 1000℃



(e) 1100℃

Fig. 6. SEM of the surface of CoO-20 at.% NiO sensor sintered at the following temperatures: (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1100 °C.

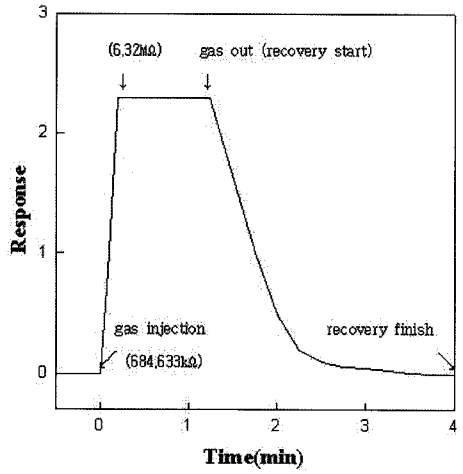


Fig. 7. Response time to i-butane gas.

sor sensitivity. Fig. 5 shows the effect of sintering temperature on sensor sensitivity to 5000 ppm butane gas for CoO-20 at.% NiO sensors. The sintering temperature of 1100 °C gives the highest sensitivity.

According to the analysis of XRD pattern, the solution phase can be obtained above 1000 °C at the given sintering time of 24 h. Aukurst and Muan[11] have found that CoO/Co_3O_4 transition temperature is 900 °C. The highest sensitivity might be due to high surface porosity as well as the presence of the solid solution phase. As shown in Fig. 6, lower sintering temperature leads to higher agglomeration between particles. The powder obtained at a low sintering temperature is so fine that it can be easily agglomerated to give low porosity, resulting in low sensitivity to butane gas.

Fig. 5 also gives the effect of sensor temperature on sensitivity to 5000 ppm butane gas for the CoO-20 at.% NiO sensors. It is found that each sensor except one sintered at 700 °C, has the highest sensitivity at the operating temperature of 250 °C.

Response and recovery times are given in Fig. 7. The sensor reveals within few seconds and 1 min in the static flow system, respectively. As compared to other hydrocarbon sensors operating above 300 °C, the recovery may be fast at 250 °C, indicating rapid adsorption and desorption of butane gas on sensor surface even at this low temperature. Long-term stability of CoO-20 at.% NiO sensor was measured for 150 days at 250 °C of the operating temperature. The sensitivity to 5000 ppm butane has changed within 10 %. Sensitivity has varied within 3 % in 60 days.

4. Conclusions

Sensitivities of NiO-CoO sensors to butane gas were investigated in terms of various binders, sintering temperature, NiO content, and operating temperature. The best sensitivity to the 5000 ppm butane is obtained for 20 at.% NiO-CoO sensors with 15 wt.% ethylene glycol binder sintered at 1100 °C at the operating temperature of 250 °C.

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