NiO(Co_{0.25}Mn_{0.75})₂O₃ and BaSrTiO₃ thick films on alumina substrate as temperature and humidity ceramic multisensors

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Abstract

NiO·(Co_{0.25}Mn_{0.75})₂O₃(Mn-Ni-Co) and Ba_{0.5}Sr_{0.5}TiO₃(BST) thick films were screen printed on Pt patterned alumina substrate to investigate the effects of sintering temperature on humidity and temperature sensing properties of ceramic sensors. A raise in sintering temperature increased resistance and B constant of the Mn-Ni-Co temperature sensor. This may have derived from the synergic effects of the reduction in charge carriers caused by the substitution of Co for Mn as well as the formation of microcracks from the difference in thermal expansion coefficients. Dependence of resistance on humidity of the Mn-Ni-Co temperature sensor, however, was not found. BST films sintered at temperatures in the range of 1100 °C to 1150 °C showed excellent humidity sensing properties. The BST humidity sensor was faster in its response than the Mn-Ni-Co temperature sensor. The humidity sensor, however, proved to be unstable under various temperatures, suggesting a need for a temperature stabilizing device. In contrast, the Mn-Ni-Co temperature sensor was stable under humid conditions.

Key Words : thick films, Mn-Ni-Co, Ba_{0.5}Sr_{0.5}TiO₃, temperature sensor, humidity sensor, alumina substrate

1. Introduction

Metal oxides exhibit an assorted and appealing class of materials whose properties cover metal, semiconductors, insulators and everything in between, affecting almost all aspects of material science and physics^[1,2]. The development of chemical and biological sensors have been fueled by an increased demand for small, economical and reliable sensors that incorporate the well-known “3S” capabilities, which are sensitivity, selectivity and stability, in such areas as environmental monitoring, toxic chemical gas detection, biomedical diagnosis and public security. In response to the needs for quicker and more reliable detection, the technology of nano-scale sensors have advanced dramatically using nanowires, nanotubes and nanofibers^[3-5].

Nowadays, sensors that used to detect temperature, gas and humidity separately are combined into a single chip, creating multi-functional sensors^[2]. These sensors can be made from two distinct materials: ceramic and

polymer. Ceramic type sensors, however, demonstrate better chemical stability, reliability and faster response^[6]. Ceramic-type temperature-humidity multi-sensors in a single chip are examined in the present study. A NiO·(Co_{0.25}Mn_{0.75})₂O₃(Mn-Ni-Co) type transition metal oxide is used for a temperature sensor due to its negative temperature coefficient(NTC) while a Ba_{0.5}Sr_{0.5}TiO₃ (BST) is used for a humidity sensor due to its positive temperature coefficient(PTC)^[1,2,6-9].

Mn-Ni-Co and BST, the two different ceramics, are used for the temperature-humidity multi-sensors, of which thick filmed ones are prepared to investigate the effect of sintering temperature on electrical properties of the sensors. In the experiment, two metal oxide pastes are screen-printed on the Pt IDT patterned alumina substrate to examine the relationships between resistance and temperature as well as between resistance and humidity. In addition, crystal structure and microstructure of the sensors are further scrutinized to elucidate the dependence of temperature and humidity on the performance of the sensors.

2. Experiment Procedure

The preparation procedure of the thick-film type ceramic temperature-humidity sensor is summarized in

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Fig. 1. A flow chart illustrating the manufacturing process of thick-film type temperature-humidity ceramic sensor.

Fig. 1. Alumina ($6 \times 15 \text{ mm}^2$, kocera, Japan) was used as a substrate. The surface of the alumina was cleaned by sonicating using an acetone. After screen printing, the Pt IDT patterned alumina was treated for 10 min at 1300°C . For the temperature sensor, powders of MnCO_3 , NiO and Co_3O_4 (aldrich Inc., USA) were used to prepare the composition of $\text{NiO} \cdot (\text{Co}_{0.25}\text{Mn}_{0.75})_2\text{O}_3$. The powders were mixed by a ball-mill with zirconia balls for 6 h. After drying, the mixed powders were calcined for 2 h at 800°C . BaTiO_3 (aldrich Inc., USA) and SrTiO_3 (ferro co., USA) powders were ball-milled for 6 h to synthesize BST. The weight ratio of ethyl cellulose/di-ethylen glycolmono butylether was 1/9 of the binder. And the ratio of power and binder was 1/2. The prepared pastes were then screen-printed onto the Pt patterned alumina substrate. After drying, the samples were sintered for 1 h at temperatures from 1050°C to 1200°C .

The crystal structure and the morphology of the samples were examined using an X-ray diffraction (XRD) and a scanning electron microscope (SEM). The dependence of temperature on resistance of the temperature sensor was monitored by using a multimeter. The variation of humidity with time was also measured. The relative humidity (RH) is the ratio of actual vapor pressure to the saturation vapor pressure and is expressed from 0 %RH to 100 %RH^[6,9]. The dependence of resistance on humidity of the sensors were evaluated by measuring resistance of a saturated 2 L-vessel contain-

ing standard solution of 400 mL under 11 %RH to 93 %RH. The RH values of the standard solutions are determined from the RH tables. The effect of temperature was also investigated at temperatures from 20°C to 60°C under 70 %RH.

3. Results and Discussion

3.1. Mn-Ni-Co temperature sensor

The dependence of temperature on resistance of the Mn-Ni-Co thick-film temperature sensor is shown in Fig. 2. As the sintering temperature rose, the resistance of the sensors decreased linearly, an indication of a typical NTC^[1,2]. Although the as-dried thick film was not sintered, it showed a similar behavior as those that were sintered. This NTC observation is depicted in Fig. 2. The relation between resistance and temperature is derived from an Arrhenius equation of $R = R_0 \exp(B/T)$. The B constant and resistance (R) of the Mn-Ni-Co thick film as functions of sintering temperature (T) are displayed in Fig. 3. As the sintering temperature increased, the B constant and resistance were raised as well. When Ni^{+2} was added to Mn_3O_4 (AB_2O_4 , $\text{Mn}^{+2} [\text{Mn}^{+3}]_2\text{O}_4$, spinel structure), Ni^{+2} substituted Mn^{+3} of site B metal. Therefore, Mn^{+3} was likely to release electron in order to maintain charge neutrality, resulting in Mn^{+4} as expressed in eq. (1). The substitution of Ni^{+2} for Mn^{+3} caused the charge imbalance, resulting in the variation of conduction. The addition of Co^{+2} , as given in eq. (2), occupied the B site at high temperatures. During the

Fig. 2. Resistance-temperature curves of the Mn-Ni-Co thick-film temperature sensors that were dried and subsequently sintered at various temperatures.

Fig. 3. Resistance and B constant of the Mn-Ni-Co thick films as a function of sintering temperature.

cooling process, the substitution of Co⁺² for Mn³⁺ resulted in accepting electron, increasing resistance caused by the decrease in charge carriers. The higher resistance and B constant were observed from the Mn-Ni-Co temperature sensors, as depicted in Fig. 3.

XRD patterns of the Mn-Ni-Co temperature sensors that were sintered at the range from 800 °C to 1200 °C are given in Fig. 4. The crystal structure of spinel (JCPDF-24-0734), as indicated by sharper and intense peaks, showed a growth along with the rise of the sintering temperature. SEM images of the surface of the Mn-Ni-Co thick film sensors are presented in Fig. 5. As sintering temperature increased, the particles agglomerated and grew in size. Microcracks are visible in Fig. 5(C) probably due to the difference in thermal expansion

Fig. 4. XRD patterns of the Mn-Ni-Co thick-film type temperature sensors that were sintered at (A) 800 °C, (B) 1100 °C, and (C) 1200 °C.

Fig. 5. SEM images of Mn-Ni-Co thick-film type temperature sensors that were (A) dried and subsequently sintered at (B) 1100 °C, and (C) 1200 °C. Note that the bar scale is 2 mm.

coefficients. As the grain size rose when increasing the sintering temperature, the resistance was likely to be raised from the reduction in charge carriers caused by the substitution of Co for Mn, as demonstrated in Fig. 3.

The resistance variation of the Mn-Ni-Co thick-film type temperature sensors at temperatures from 25 °C to 80 °C and *vice versa* is depicted in Fig. 6. The response

Fig. 6. Response of resistance plots for the Mn-Ni-Co thick-film type temperature sensors sintered at 1100 °C. Note that the temperature was varied from 25 °C to 80 °C and *vice versa*.

Fig. 7. Dependence of resistance on humidity of the Mn-Ni-Co temperature sensors sintered at 1100 °C, 1150 °C, and 1200 °C.

times of the sensors at temperatures from 25 °C to 80 °C and from 80 °C to 25 °C were 90 s and 300 s with resistance deviations of 150 kW and 145 kW, respectively. The sensors exhibited the longer response time(300 s) during the cooling process and a shorter response time of 90 s during the heating process. Higher variation in resistance at low temperature regime(25 °C~80 °C) is observed in Fig. 6. Dependence of resistance on humidity of the temperature sensor was not detected, as shown in Fig. 7. Therefore, the Mn-Ni-Co temperature sensor can be highly applicable to the multi-sensors in a single chip.

3.2. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) humidity sensor

In perovskite type oxides(ABO_3 , BaSrTiO_3), the atoms on site A were susceptible to humidity^[6]. Perovskite structure was positive ionic conductor at room temperatures. The dependence of resistance on RH of the BST humidity sensor sintered at temperatures from 1050 °C to 1200 °C is shown in Fig. 8. Unlike the sensors that were sintered at 1050 °C, the resistance of the sensors increased with raising sintering temperatures from 1100 °C to 1200 °C. The resistance of the BST humidity sensors decreased with the rise of RH. The effect of sintering temperature on density and resistance of the sensors at 11 % RH was evaluated and is shown in Fig. 9. Resistance variation of the BST humidity sensor is likely to be due to the formation of oxygen vacancies and density variation^[6,9]. As temperature rose upto 1150 °C, resistance increased as a result of the decrease in oxygen vacancies. Because of higher density, the

Fig. 8. Resistance of the thick-film type humidity sensors as a function of relative humidity. Note that the sensors are sintered at temperatures in the range of 1050 °C to 1200 °C.

Fig. 9. Resistance and apparent density of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thick film type humidity sensors measured at 11 %RH as a function of sintering temperature.

resistance decreased slightly when sintering temperature was higher than 1150 °C, as depicted in Fig. 9. Charge transport mechanism as a function of RH is explained by Grotthuss's chain reaction^[6,9]. Negatively charged oxygen was electrostatically attached to the positively charged Ba^{+2} ions of the BST sensor. The initial monolayer was chemisorbed between Ba^{+2} and oxygen of the water layer($\text{Ba}^{+2} + \text{H}_2\text{O} \rightarrow \text{Ba}^{+2} - \text{OH} + \text{H}^+$). Once the first layer was formed, subsequent layers of water molecules were physically adsorbed. This physisorbed water molecules dissociated due to the high electric fields in the chemisorbed water layer. The charge transport occurred when H_3O^+ ions released a proton to neighboring water molecules, which accepted it while releasing another proton and so on($2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$). Hence called Grotthuss's chain reaction^[9].

Fig. 10. SEM images of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thick-film type humidity sensors that were (A) dried and subsequently sintered at (B) 1100 °C, and (C) 1200 °C. Note that the bar scale is 2 mm.

It was found that the resistance decreased with the temperature rising above 1200 °C, as displayed in Fig. 9. SEM results(Fig. 10) revealed that the size of grains and pores grew with increasing the sintering temperature. A larger pore size may be detrimental to sensitivity of the sensors due to the adsorption of water molecules. XRD results of the BST sintered for 1 h at temperatures from 1100 °C to 1200 °C are presented in Fig. 11. The XRD pattern of the

Fig. 11. XRD patterns of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thick-films that were (A) dried and subsequently sintered at (B) 1100 °C, and (C) 1200 °C.

Fig. 12. Response time of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thick-film type humidity sensor sintered at 1150 °C.

BST sample sintered at 1200 °C is attributed to single perovskite BST structure(JCPDS-31-0174).

The resistance variation of the BST thick-film type humidity sensors sintered at 1150 °C at RH from 32 % to 85 % and *vice versa* is depicted in Fig. 12. The average response times of the sensors at RH from 32 % to 85 % and *vice versa* were 60 s and 120 s with resistance deviations of 225 MW and 208 MW, respectively. The response times of the BST humidity sensors were faster than those of the Mn-Ni-Co temperature sensors. However, the resistance of the humidity sensors was susceptible with the change of the working temperature, as can be seen in Fig. 13. Therefore, it is conceivable that a temperature compensating device should be applied to the present humidity sensor for the sensor stabilization.

Fig. 13. Dependence of temperature on resistance of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thick-film type humidity sensor at 70 %RH. Note that the sensor is sintered at 1100 °C.

4. Conclusion

Mn-Ni-Co and BST thick films are screen printed on IDT Pt patterned alumina substrate to investigate the effect of sintering temperature on humidity and temperature sensing properties of the sensors. A raise in sintering temperature increased resistance and B constant of the Mn-Ni-Co temperature sensor. This may have derived from the synergic effects of the reduction in charge carriers caused by the substitution of Co for Mn as well as the formation of microcracks from the difference in thermal expansion coefficients. Dependence of resistance on humidity of the Mn-Ni-Co temperature sensor, however, was not found. BST films sintered at temperatures in the range of 1100 °C to 1150 °C showed excellent humidity sensing properties. The BST humidity sensor was faster in its response than the Mn-Ni-Co temperature sensor. The humidity sensor, however, proved to be unstable under various temperatures, suggesting a need for a temperature stabilizing device. In contrast, the Mn-Ni-Co temperature sensor was stable under humid conditions.

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