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Structural and electrical properties of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick-film bolometer with addition of copper (Cu) for application in infrared sensors

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In this study, $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ ($0 \le x \le 0.15$) thick films were coated on alumina substrate using a screening printing technique. All specimens were sintered in air at 1150 °C for 6 hr and annealed at 830 °C. We investigated structural and electrical properties with variations of Cu amount. The results from using a screening printing technique have been shown that all specimens were in a cubic spinel phase formation without any second phase. Our study also found that the electrical resistivity at room temperature and the TCR were decreased as the Cu amount was increased. The $Ni_{0.79}Mn_{2.11}Cu_{0.10}O_4$ thick film showed higher electrical properties than any other $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film. The resistance at room temperature, TCR, responsivity and detectivity of $Ni_{0.79}Mn_{2.11}Cu_{0.10}O_4$ thick films were 353 Ω-cm and 3.61%/°C, 0.0212 V/W and 1.25×10^4 cmHz$^{1/2}$/W, respectively.

Key words: Cubic spinel, Screening printing, TCR, Responsivity, Detectivity.

Introduction

Infrared sensors have mainly been used for special purposes such as military or medical use for a longtime. Recently, in addition to these special purpose applications, they have been widely used in various other forms such as single sensors or optical couplers in industrial safety, security, or surveillance systems, civilian electronic devices, etc [1]. Even though a bolometer, which is a thermal type detector among infrared sensors, has relatively lower responsivity and detectivity compared to those of photon type sensors, it has some advantages over these types of sensors. For example, a Bolometer can be operated at low temperatures and has lower production costs [2]. At present, vanadium oxide is the most commonly used main material for bolometers. However, bolometers using vanadium oxide can only be used at temperatures 50 °C due to their instability when they are operated at temperatures above 50 °C. Therefore, many materials are being developed to extend their operation temperature ranges [3], and, among them is Ni-Mn ceramic, which has a spinel structure and is known to be structurally stable up to 300 °C due to its high temperature coefficient resistance(TCR) value [3]. However, because Ni-Mn ceramic has a high specific resistance at room temperature, it generates high volume noise when applied to a bolometer.

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In this study, we plan to prepare a Ni-Cu-Mn thick-film that has high TCR and low specific resistance by adding a small amount of copper impurity (Cu) to the Ni-Mn ceramic. Cu^{2+} of 0.00 ~ 0.15 mol % was added to the best $Ni_{0.79}Mn_{2.21}O_4$ composition, which was obtained in a previous result [4]. The $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick-film was deposited on an alumina substrate using the screen printing method, and then thick-film's microstructural change and electrical property were analyzed according to the Cu^{2+} content to determine its applicability as an infrared sensor bolometer.

Experimental

During this study MnO (99%), NiO (99%), and CuO (99%) were used as starting materials, and the mixing ratio for each of the materials was $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$. First, each material was pre-weighed according to the composition above and ball-milled using zirconia balls and ethanol as the dispersing medium in wet condition for 24 hours. After ball milling, it was dried at 100 °C in an oven for 24 hours and then the dried powder was calcined at 900 °C for 2 hours. After re-grinding the calcined powder, a paste was prepared by mixing it with organic binders. The prepared$Ni_{0.79}Mn_{2.21-x}Cu_xO_4$paste was coated four times by the screen printing method on a 15 × 15 × 0.58 mm alumina substrate where platinum (Pt) electrodes were deposited. After coating, the prepared think-film was dried at 400 °C and sintered at 1150 °C for 6 hours, and then the desired $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$thick-film sample was prepared by fast cooling from 830 °C in order to form the spinel structure.

The crystallinity of the $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick-film prepared by the screen printing method was analyzed using an X-ray diffraction (XRD) instrument and a field emission scanning electron microscopy (FE-SEM) was used to analyze the surface and cross-section microstructures of the deposited thick-film. Electrical properties were measured from −10 °C to 60 °C at 2 °C intervals using a digital multi-meter and the infrared detection capability was investigated by utilizing an IR Detector.

Results and Discussion

Fig.1 shows results of X-Ray diffraction analysis of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ samples with the addition of Cu. It was confirmed that a single cubic spinel phase without a secondary phase was formed in all samples.

Fig. 2 and 3 depict the surfaces and cross-section (thick-film/electrodes/alumina) microstructures of the $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$sampleswith the addition of Cu. It can be seen that most of the pores exist along the grain boundary and that a secondary phase is not generated

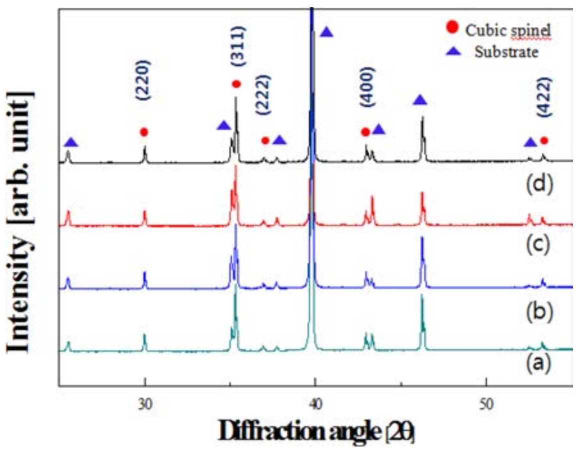

Fig. 1. X-Ray Diffraction pattern of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.10 (d) x = 0.15.

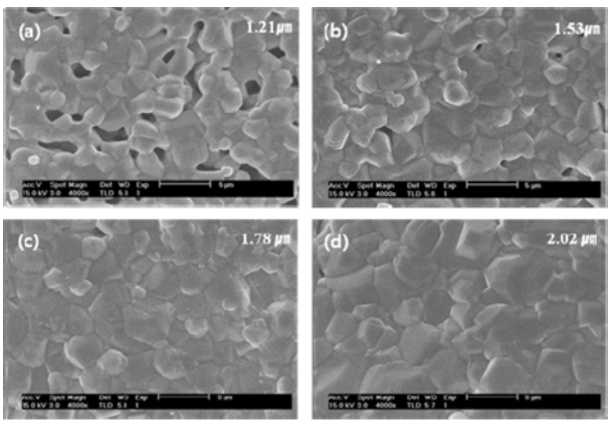

Fig. 2. FE-SEM surface image of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.10 (d) x = 0.15.

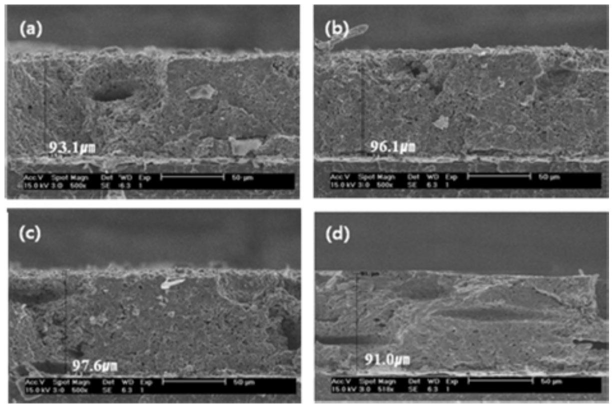

Fig. 3. FE-SEM Cross-section image of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.10 (d) x = 0.15.

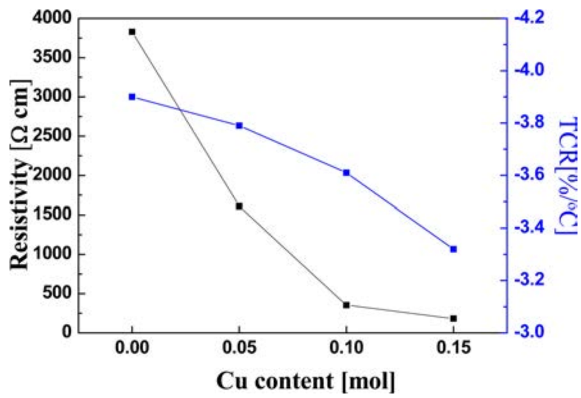

Fig. 4. Resistivity at room temperature and TCR of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.10 (d) x = 0.15.

by neither segregation nor interface reaction at the thick-film/electrodes interface or at the thick-film/alumina substrate interface. It is confirmed that the crystal grains become denser as they increase in size from 1.21 μm to 2.02 μm as Cu^{2+}content increases. This is believed to be because the movement of the material is promoted by liquid phase sintering as the Cu content, which has lower melting point, increases.

Fig. 4 shows specific resistance and TCR values at room temperature with the addition of Cu. As the Cu content increases, specific resistance at room temperature decreased from 3830Ω-cm to 185Ω-cm. This is explained by the hopping of the spinel structure. Once Cu is added to the $NiMn_2O_4$ structure, Mn^{2+}at the A-site of the spinel structure is substituted by the Cu^{2+}. As Cu content increases, Mn^{3+}at the B-site is substituted by the remainingCu^{2+}, and thus Mn^{4+} forms. That is, the specific resistance is decreased due to the increase of both $Mn^{3+}$and Mn^{4+}that can contribute to the hopping [5].

$$TCR = \frac{1}{R}\frac{dR}{dT}(\%/°C) \quad (1)$$

TCR property, which is the rate of change in resistance with change in temperature, can be obtained by equation

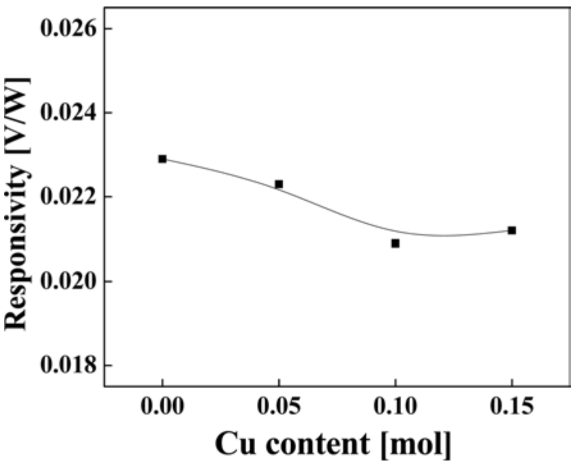

Fig. 5. Responsivity of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.10 (d) x = 0.15.

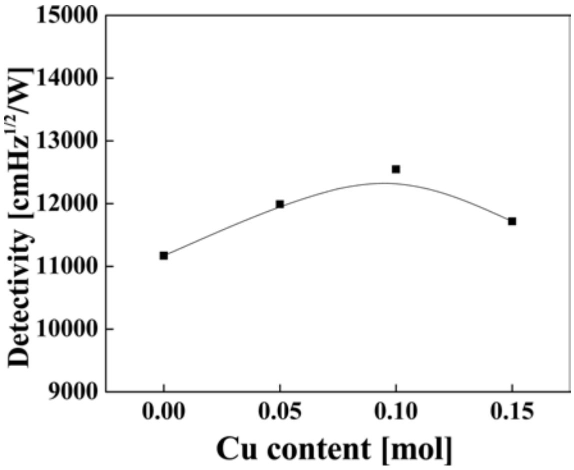

Fig. 6. Detectivity of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x= 0.05 (c) x = 0.10 (d) x = 0.15.

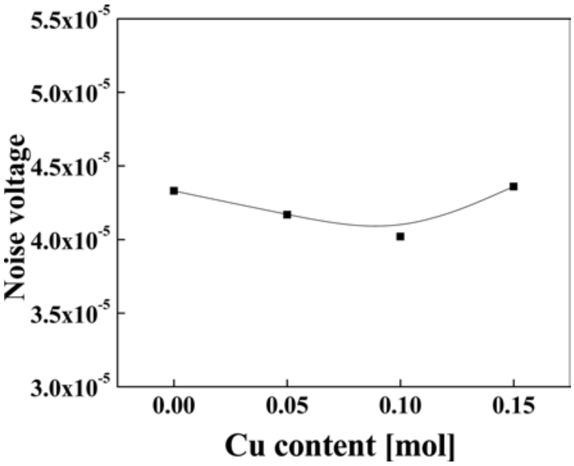

Fig. 7. Voltage noise of $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick film with variation of Cu content: (a) x = 0 (b) x = 0.05 (c) x = 0.1 (d) x = 0.15.

(1), where R is resistance of the thick-film and T is temperature. As the Cu content increases, TCR is decreased, but is relatively high at 3.0%/°C or higher. As equation (1) shows, the TCR decreases when the resistance decreases due to increasing Cu content.

Table 1. Bolometer measuring parameter.

Measuring parameter	
Wavelength	8-12 °μm
BBS temperature	500 °C
BBS apetrure	1”
Bias voltage	1 V
Grain	10
MF	2 Hz

Responsivity is the change in the output signal according to changes in the incident infrared and it can be expressed by the following equation [6].

$$R_v = \frac{\varepsilon \alpha R_b I_b}{G_c \sqrt{(1+\omega^2\tau^2)}} (V/W) \quad (2)$$

Fig. 5 shows the responsivity of the$Ni_{0.79}Mn_{2.21-x}Cu_xO_4$thick-film according to the Cu content. It shows a trend of gradual decreases as the Cu content increases. This is likely due to the decreases in both the specific resistance (R_b) and TCR (α)with respect to the increase of the Cu content.

Detectivity is the infrared detection capability of a device and can be represented by equation (3) below. In addition, equation (3) is an expression that represents the total noise(thermal noise, 1/f noise), which affects the detectivity of the thick-film [7].

$$D^* = \frac{R_v \sqrt{A_d \cdot BW}}{V_n} (cm\sqrt{Hz}/W) \quad (3)$$

$$\sqrt{\Delta V^2} = \sqrt{4kTR(f_2 - f_1) + V^2 K \int_{f_1}^{f_2} \frac{1}{f^\alpha}} \quad (4)$$

Fig. 6 shows the detectivity of the $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick-film according to the Cu content. Detectivity increased up to 1.25×10^{-4} $cm\sqrt{Hz}$ with the increase of the Cu content, and then decreased again. As shown by equation (3) above, detectivity should decrease in relation to the decrease of responsivity, but our study results showed that it tended to increase. This can be explained as noise characteristics in Fig. 7. As the Cu content increases, detectivity improved due to the noise reduction. Therefore, it can be determined that detectivity is more significantly affected by the effect of noise reduction due to the decrease in specific resistance than by the effect of responsivity reduction due to the decrease in specific resistance. A thick-film with 0.01 mol% Cu had the least noise (4.02×10^{-5}) and the highest detectivity (1.25×10^4 $cm\sqrt{Hz}/W$).

Conclusions

Within this study, a $Ni_{0.79}Mn_{2.21-x}Cu_xO_4$ thick-film was prepared with the addition of Cu by the screen printing method to develop an uncooled type bolometer for application as an infrared sensor. All samples prepared by fast cooling from 830 °C after sintering at 1150 °C for 6 hours, showed cubic spinel structures based on X-ray diffraction analysis. As the Cu content increased, the specific resistance dramatically decreased up to 185Ω-cm and the TCR values also decreased up to 3.2%/°C, although this is relatively high, exceeding 3.0%/°C. In addition, the decreases of the specific resistance and the TCR led to the decrease of the responsivity. Although detectivity was expected to decrease with the decrease of the responsivity, it tended to increase as the noise decreased.

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