Improvement of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($0.1 \leq x \leq 0.4$) Film Preparation and Assessment of Its Structure and Properties

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A series of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$, and 0.4) films were prepared by the chemical solution deposition method and then post-heated at 150°C for 300 h. Scanning electron microscopy and x-ray diffraction revealed remarkable improvements in relative density and crystallinity in post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$, and 0.4) films. From x-ray photoelectron and Raman spectroscopy, it was found that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio decreases after post-heating, which leads to a decrease in Raman mode intensity. Furthermore, spectroscopic ellipsometry results show that both the refractive indexes and extinction coefficients of post-heated films are higher than those of annealed films in the visible range. However, the band gaps of all the films decreased significantly after the heating process. These investigations suggest that the post-heating treatment may be preferable for fabricating $\text{Mn}_{1.56}\text{Co}_{0.96}\text{Ni}_{0.48}\text{O}_4$ thin films for optical detection.

Key words: Structure, optical properties, post-heated, films

INTRODUCTION

Manganese-based oxides with spinel structures of the general formula AB_2O_4 have been extensively utilized in thermistor devices and, especially, for bolometer infrared detectors, and for commercial and space travel applications.^{1,2} The compound $\text{Mn}_{1.56}\text{Co}_{0.96}\text{Ni}_{0.48}\text{O}_4$ has a unique composition that has a low resistivity and a high sensitivity to negative temperatures. This makes it suitable for providing optimum performance in the bolometer infrared detectors used in satellites.² The physical properties of Mn-Co-Ni-O-based materials depend on variations in the distribution of cations in the spinel structure,^{2,3} which is influenced by the composition and processing of the material.^{4–6} The effect of adding other metal cations to the structures of Mn-Co-Ni-O-based materials on their physical

properties has recently been a subject of systematic study.^{7,8} It has been reported that Al^{3+} entering Mn-Co-Ni-O grains significantly facilitates optical absorption in the $0.63\text{--}2\ \mu\text{m}$ wavelength range, which is significant in the design and application of infrared detectors.⁹

To date, $\text{Mn}_{1.56}\text{Co}_{0.96}\text{Ni}_{0.48}\text{O}_4$ (MCN) films have been fabricated by laser molecular beam epitaxy, the pulsed laser deposition method, RF magnetron sputtering, chemical solution deposition (CSD), and so on. Among these, the CSD method has attracted considerable interest in recent years as it is a simple, low-cost technology for oxide-based spintronics. The Mn-Co-Ni-O-based films fabricated by the CSD method combine the advantages of both Mn-Co-Ni-O-based ceramic bulk and thin films. Some efforts have been made to study sintering and other processes used in the CSD method that result in various oxygen stoichiometries and metal cation distributions in Mn-Co-Ni-O-based films.^{9,10} The suitable crystalline temperature of Mn-Co-Ni-O-based films is $1100\text{--}1400^\circ\text{C}$.^{11,12} However, in

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Fig. 1. SEM images of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films.

Fig. 2. XRD patterns of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films.

order to make the films match well to the substrate, films prepared by the CSD method are annealed at a temperature of 750°C. The application of films prepared by the low-cost CSD method is limited, because their quality and stability are low.^{13,14}

Advances in film preparation technology are necessary for the CSD method. Considering that temperature is the main factor affecting stability, a temperature compensation process was incorporated in our experiments.

In this paper, we prepared $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$, and 0.4) films on Si substrates by the CSD method. Then, all films were post-heated at 150°C for 300 h in an air-drying oven. Investigation of the microstructure and optical properties of the films after the post-heating process will provide useful information for optimization of the CSD method and preparation of high-quality negative temperature coefficient thin films.

EXPERIMENTAL

A series of films with compositions of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) were fabricated by a CSD method. Powders of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were mixed and dissolved in glacial acetic acid at 60°C for 1.5 h. Then, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the former solution after it had cooled to room temperature, and then was stirred with a magnetic stirrer for 2 h. The precursor solution was filtrated using a 0.45 μm syringe filter after it had sat for 24 h. A precursor solution with a concentration of 0.2 mol was then prepared. The pellucid precursor solution was spin-

coated on Si (100) substrates to form a layer of wet film. The spin coater was set at 500 rpm for 5 s and 4000 rpm for 20 s. The wet film was put into a tube furnace and heated at 350°C for 5 min to eliminate water and acetic acid. The above spin-coating and wet-film-drying procedures were repeated ten

times. Finally, all the samples were annealed at 750°C for 60 min in air. The post-heating process occurred in a drying oven at 150°C for 300 h.

The crystal structures of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films were identified by x-ray diffraction (XRD);

Fig. 3. XPS spectra of Mn 2p and their signals for the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ films ($x = 0.1$ and 0.4).

Table I. The ratios of $\text{Mn}^{3+}/\text{Mn}^{4+}$ for $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1$ and 0.4) films

	$x = 0.1$		$x = 0.4$	
	Annealed films	Post-heated films	Annealed films	Post-heated films
Mn^{2+} (%)	50.90	50.43	49.05	50.66
Mn^{3+} (%)	36.66	36.67	37.59	33.16
Mn^{4+} (%)	12.44	12.90	13.36	16.18
$\text{Mn}^{3+}/\text{Mn}^{4+}$	2.948	2.844	2.812	2.049

Fig. 4. Raman spectra of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films.

Broker D8) in the range of 20° – 60° . The surface micrographs were represented by a scanning electron microscope (SEM; Zeiss Supra55VP). The distribution of the cations in films were characterized using an x-ray photoelectron spectroscopy (XPS, Kratos). Information on chemical bonds was measured by a micro-Raman spectrometer (NRS-1000) using an Ar^+ laser (20 mW, 532 nm) with the excitation source in the backscattering configuration. The optical parameters were measured by spectroscopic ellipsometry (Sentech SE850) with an incident angle of 70° across the spectral range of 300–1800 nm. The refractive index n and extinction coefficient k were calculated using software.

RESULTS AND DISCUSSION

Figure 1 illustrates SEM micrographs of the annealed and the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films. The average particle sizes decreased significantly as the number of Al^{3+} cations increased. The $\text{Mn}_{1.56}(\text{Co}_{0.9}\text{Al}_{0.1})_{0.96}\text{Ni}_{0.48}\text{O}_4$ and $\text{Mn}_{1.56}(\text{Co}_{0.8}\text{Al}_{0.2})_{0.96}\text{Ni}_{0.48}\text{O}_4$ films were quite dense. However, the other films had a porous microstructure. This demonstrates that the compactness deteriorates after the addition of Al^{3+} cations in the MCN films. Although the post-heating process had no influence on the sizes and shapes of

the grains, all the films became much denser and more compact after post-heating.

The XRD patterns of the annealed and post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films deposited on Si (100) substrates are shown in Fig. 2. Spinel structures were observed for all films by making reference to NiMn_2O_4 with the PDF card no. 84-0542, showing four distinct peaks. This demonstrates that Al^{3+} cations had been diffused into the Mn-Co-Ni-O lattice to form a homogeneous solid solution. The corresponding diffraction peaks of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films become sharper and stronger after post-heating, which indicates a further improvement in their crystallinity. In addition, all the peaks shifted slightly towards lower 2θ angles after the heating process. Such features are related to cation redistribution and lattice expansion.¹⁵ In Mn-based spinel materials, the lattice constant, as well as physical properties, are mainly affected by changes in the variation of the manganese ion octahedral and tetrahedral distributions.¹⁶

In order to compare the variation in the valence states of manganese between the annealed and the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films, the XPS spectra for the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.4$) films were measured, as shown in Fig. 3. For $x = 0.1$, the Mn 2p XPS peaks of the annealed and the post-heated films were not significantly different. However, for $x = 0.4$, the peaks of Mn 2p were heightened and attained a greater binding energy after the post-heating process. This illustrates that the average state of the Mn in the post-heated films was higher than that of the annealed films. After experimental data normalization, we analyzed the $\text{Mn}2p_{3/2}$ XPS spectra of the films by applying a peak synthesis procedure, as per Fig. 3b–e, and summarized the relative concentration of Mn^{3+} (642.8 eV) and Mn^{4+} (644.2 eV) cations in Table I.¹⁷ It can be seen that the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios were 2.948, 2.844, 2.812, and 2.049 for the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1$) film, the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1$) film, the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.4$) film, and the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.4$) film, respectively. Even after adding Al^{3+} cations, there was little

Fig. 5. (a) The fitting values of $\tan(\Psi)$ and $\cos(\Delta)$, (b) the refractive index n , and (c) the extinction coefficient k of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films.

change in the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. The $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios of the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films were lower

than those of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films, which will lead to different physical properties.

Fig. 6. The plots of $(\alpha h\nu)$ versus $(h\nu)$ for $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films, and E_g values are estimated by tangents.

Raman spectroscopy can provide useful information on the crystal orientation of thin crystal films. A series of $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) film Raman spectra were measured at room temperature in the range $200\text{--}900\text{ cm}^{-1}$ (Fig. 4). The main vibration mode (A_{1g}) was located at around 620 cm^{-1} , which is associated with the symmetric $[\text{Mn}^{3+}\text{-O}]$ stretching vibration in the octahedral unit of $[\text{Mn}^{3+}\text{-O}]_6$.^{18,19} The Raman peaks located at around 500 cm^{-1} are assigned to the F_{2g} mode, which originates from the symmetric bending vibration of $[\text{Mn}^{4+}\text{-O}]$ bonds.²⁰ The positions, and the intensities of the A_{1g} and F_{2g} modes for $x \leq 0.2$ showed little difference between the annealed and post-heated films. However, the intensities of both the A_{1g} and F_{2g} modes of the $x \geq 0.3$ post-heated films decreased and shifted to the right due to the mean grain size of the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ films ($x \geq 0.3$) decreasing after the post-heating process.

A three-layer model (air/ $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films/substrate) was built, and the Tauc-

Lorentz oscillator dispersion relationship was used for fitting and calculating the optical parameters. Two important ellipsometry parameters (Ψ and Δ) were measured at room temperature, and are related to the physical amplitude and phase, respectively. The fitted values of $\tan(\Psi)$ and $\cos(\Delta)$ in the wavelength range of $300\text{--}1800\text{ nm}$ are shown in Fig. 5a. The model fitting was implemented by minimizing the mean square error (MSE) function defined as²¹:

$$\text{MSE} = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi_i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta_i}^{\text{exp}}} \right)^2 \right] \quad (1)$$

where N is the number of (Ψ, Δ) pairs, M is the number of variable parameters in the model, σ is the standard deviation of the experimental points, and the superscripts *mod* and *exp* denote the calculated and experimental values, respectively. The mean square error values for the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and

0.4) films (and aged films) were 0.3356 (0.2642), 0.2898 (0.2257), 0.2722 (0.3285), and 0.7816 (0.8230) for $x = 0.1, 0.2, 0.3$, and 0.4 , respectively. The optical constant refractive index n and extinction coefficient k were calculated as follows²²:

$$n = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1} \quad (2)$$

$$k = \frac{1}{\sqrt{2}} \sqrt{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1} \quad (3)$$

where ε_1 and ε_2 are the real and imaginary components of the complex dielectric, respectively.

The refractive index n of films in the range of 300–1800 nm are presented in Fig. 5b. The curves of the four films display trends that increase with wavelength. The refractive index n of each $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) film had a peak after 900 nm, except for the $x = 0.4$ films. This is because the $x = 0.4$ films have more numerous small particles than the others.¹⁶ Moreover, the curves n of the post-heated films were higher than the annealed films in the visible wavelength range (380–780 nm).

According to Fig. 5c, the extinction coefficient k curves have two peaks in the range of 300–1800 nm. The difference between the n and k curves increases as the Al^{3+} content increases. The peaks of the post-heated films were higher than the annealed films at wavelengths below 950 nm, indicating that the post-heating treatment can enhance the films' absorption in the visible range. The k curves of the $x = 0.2$ and 0.4 post-heated films decreased compared with the annealed films after 950 nm. For the post-heated films, the peaks of the k curves shifted slightly to smaller wavelengths.

The band gap, E_g , of all the $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films can be calculated by the Tauc equation: $(\alpha h\nu)^2 \propto A(h\nu - E_g)$, in which the absorption coefficient, α can be determined by the Kramers–Kronig transformation: $\alpha = \frac{4\pi k}{\lambda}$ and A is a constant.^{23–27} Figure 6 shows a plot of $\alpha h\nu$ versus $h\nu$ for the annealed and the post-heated films, illustrating that the absorption coefficients of all the films increase as a function of the photon energy. By extrapolating the straight-line portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to the photon energy axis, we obtain E_{gA} values for the annealed $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films of 3.20, 3.33, 3.22, and 2.91 eV for added- Al^{3+} contents of 0.1, 0.2, 0.3, and 0.4, respectively. The corresponding E_{gP} values of the post-heated $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films were 3.07, 3.05, 2.94, and 2.84 eV. This demonstrates that the band gaps of all four $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films decreased after the post-heating process.

CONCLUSIONS

$\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ ($x = 0.1, 0.2, 0.3$ and 0.4) films were fabricated by the CSD method and then post-heated. The structural and optical properties of the annealed and the post-heated films were investigated, which showed that crystallinity and relative density improved after post-heating. The refractive index n and the extinction coefficient k values of the post-heated films were greater than those of the annealed films in the visible range, especially for $\text{Mn}_{1.56}(\text{Co}_{1-x}\text{Al}_x)_{0.96}\text{Ni}_{0.48}\text{O}_4$ films with $x = 0.3$ and 0.4 . Furthermore, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio decreased in the post-heated films, leading to significant decreases in the Raman mode intensity and band gap.

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