Electrical properties and stability of low temperature annealed (Zn,Cu) co-doped (Ni,Mn)\textsubscript{3}O\textsubscript{4} spinel thin films

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ABSTRACT

Toward the development of infrared (IR) detectors, nickel–manganite-based thin films were initially prepared from (Ni\textsubscript{0.3}Mn\textsubscript{0.7}Cu\textsubscript{0.1})Cl\textsubscript{2} (0.010 ≤ x ≤ 0.040) solutions using the liquid flow deposition (LFD) method. The influence of Cu on the negative temperature coefficient of resistance (NTCR) characteristic of the films annealed at 400°C was investigated. It was found that the incorporation of Cu can effectively enhance electrical conductivity; however, it degrades both the thermal sensitivity and stability of the nickel–manganite films. The investigation was extended by further modifying the composition with Zn. The results revealed that by co-doping Cu with a proper amount of Zn the temperature coefficient of resistance (TCR) could be tailored, while a relatively low resistivity (ρ) of the final products was retained. Specially, when 0.01 mol Zn was added to a precursor solution containing 0.025 mol Cu, the resulting specimen possessed a TCR = 2.82% K\textsuperscript{-1} and a ρ = 820 Ω (measured at RT). More importantly, compared to Zn-free films, the (Zn,Cu) co-doped compositions showed much improved electrical stability, with an aging coefficient (ΔR/R) as low as 4.6%, after aging at 150°C in air for 500 h. The results suggest that the (Zn,Cu) co-doped (Ni,Mn)\textsubscript{3}O\textsubscript{4} thin films have a promising application in IR detectors.

1. Introduction

Nickel manganite oxide ceramics, which exhibit a negative temperature coefficient of resistance (NTCR) characteristic, have been attracting substantial attention for several decades [1,2]. These materials have been used for infrared sensing applications because of their high-temperature sensitivity, fast response, cost-effectiveness, adaptable size, and practical convenience [3,4]. The nickel manganite system has a spinel-type structure with the general formula AB\textsubscript{2}O\textsubscript{4} (A: tetrahedral and B: octahedral sites), and conduct electricity through electron hopping between the Mn\textsuperscript{3+} and Mn\textsuperscript{4+} states at the B sites [1,3,5].

One feasible way to approach the electrical conductivity is to modify the nickel manganite compounds with transition metal ions [6]. In particular, the partial replacement of Mn ions by other appropriate ions at both the A and B sites alters the spinel structure from its normal state to a mixed state, which enhances the possibility for Mn to adopt multiple oxidation states; and consequently induces the charge carriers [7,8]. Among the transition elements, Cu is the most effective for enhancing the conductivity of nickel manganites due to the insertion of monovalent copper (Cu\textsuperscript{1+}) ions into the A sites, which leads to the displacement of Ni\textsuperscript{2+} cations from the A sites to the B sites of the spinel structure [9–11].

In general, under thermal constraint, most NTCR ceramics undergo an increase in electrical resistance over time, known as “aging” [12,13]. The aging characteristic is presented by resistance drift (ΔR/R, %) that reflects the electrical stability of the materials. An ΔR/R in the range of 2–20% has been reported for conventional nickel–manganite ceramics [14]. In practice, the IR devices require detecting materials with a low electrical resistivity (ρ < 3 kΩ cm) and a large temperature coefficient of resistance (TCR > 2%K\textsuperscript{-1}) [2,4]. However, to maintain the reproducibility of ρ and TCR, the materials should be highly stable, as well. Although Cu benefits the electrical properties, this element otherwise degrades the electrical stability of the nickel manganites [6,15,16]. Chen et al. reported that Cu caused a remarkable decrease in the resistivity from 2907 to 12.6 Ω cm for Ni\textsubscript{0.3}Mn\textsubscript{0.7}O\textsubscript{4} ceramics, but simultaneously raised an increase in ΔR/R up to 14.9% [17]. Such a poor electrical stability limits the use of those ceramics in commercial products. Fritsch et al. observed a change in the resistance of Ni\textsubscript{0.3}Mn\textsubscript{0.7}O\textsubscript{4} ceramics that were separately aged at 125°C in nitrogen and air [13]. The authors found that the ceramics aged under nitrogen exhibited a nearly unchanged resistance, while it was notable in the samples exposed to air. The results suggested that aging phenomena is
primarily driven by ceramic oxidation occurring during metallization.

The composition of materials has been reported to play a decisive role to the oxidation [18]. Hence, various ions have been added into nickel manganites in different ways to improve the electrical stability. Notably, partially replacing manganese (Mn) with zinc (Zn) has been illustrated to effectively stabilize the spinel structure against the oxidation reactions [19,20]. Ma and co-workers observed a decrease of $\Delta R/R$ from 10.2% to 0.02% by doping 0.75 mol Zn to Ni$_{0.6}$Cu$_{0.5}$Mn$_{1.0}$O$_4$ ceramics [21]. The authors also found that Zn doping can otherwise improve the thermal constant ($\delta$) of the ceramics. Due to the great benefits of Cu and Zn on the electrical properties, the ceramics with Mn–Ni–Cu–Zn–O composition have become one of the most important NTCR materials.

The electrical and physical properties of NTCR nickel manganite have been widely studied, but most researchers focused on bulk and thick-film forms. Unfortunately, poor stability and reproducibility are commonly observed for bulk ceramics due to the porous and non–dense structure [22], while thick films often show low sinterability [23]. Otherwise, both the bulks and thick films commonly require sintering temperatures above 1000°C [16,17,19,20,22,23] that is too high for the modern electronic applications. These shortcomings can be overcome by use of dense polycrystalline thin films prepared at low temperatures. Devices integrated with thin films also exhibit other advantages, such as faster output response and lower operating voltages [1,3]. Furthermore, the major trend of current electronics technology is to reduce the dimensions of electronic components, thus fabricating passive components using thin-film techniques is an emerging solution.

Thin films can be prepared using various methods, of which the chemical solution routes have attracted considerable attention because of their simplicity and large area coverage. Actually, the films prepared from solutions commonly require a post annealing process for crystallization, so as to improve their electrical conductivity and stability. Obviously, the annealing temperature should be as low as possible to avoid any practical difficulties during the integration process. For example, in the microbolometer industry the typical temperature must be less than 400°C to maintain the compatibility with CMOS [16]. In the last ten years, many studies have been conducted on nickel–manganite thin films, exploring their electrical mechanism by various techniques however, the crystallization only occurs at firing temperatures above 500°C [1,4].

In 2015, we discovered that by exploiting Mn$^{2+} \rightarrow$ Mn$^{3+}$ oxidation in aqueous solution, nickel–manganite-based thin films can be synthesized by liquid flow deposition (LFD) method [24]. We then prepared thin films of (Co,Ni,Mn)$_3$O$_4$ cubic spinel–type oxides with excellent electrical properties [25]. In the present study, the LFD was extended to grow (Ni,Mn)$_3$O$_4$ thin films doped with Zn and Cu. In particular, we demonstrated the effects of Zn and Cu co-doping on the morphology, phase, electrical properties and aging behavior of the (Ni,Mn)$_3$O$_4$-based thin films annealed at 400°C.

2. Experimental procedure

The reaction solutions were prepared with the chemical formula (Ni$_{0.8}$Mn$_{2.8-x}$xCu$_x$Zn$_{2.0}$)Cl$_2$ with $x =$ 0.000, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, and 0.040; $y =$ 0.000, 0.005, 0.008, 0.010, 0.012, and 0.015. MnCl$_2$ · 4H$_2$O, NiCl$_2$ · 6H$_2$O, CuCl$_2$ · 2H$_2$O, and ZnCl$_2$ · 4H$_2$O (Sigma-Aldrich) with purity $>$ 98% were used as the starting materials. The compounds were firstly dissolved in deionized (DI) water, forming solutions with concentrations of 50 mM. An appropriate amount of NH$_4$Cl was admixed to solutions during stirring. The solutions were then stirred 2 h more before being used for deposition.

The glass substrates (2.5 x 2.5 cm$^2$) were immersed in a piranha solution, H$_2$O$_2$/H$_2$SO$_4$ = 3/7 (volume ratio) at 80°C for 1 h. The substrates were then naturally cooled and washed in the following solvents in the order of DI water, ethanol, and methanol to remove any residual contamination. Finally, they were kept in an oven at 120°C for 12 h to allow hydroxyl groups to form on their surface [26].

The LFD thin-film deposition process was described in detail in our earlier study [24]. In the present work, ammonia (NH$_3$/H$_2$O) was used to adjust the pH in a range of 6.55–6.85. The film was deposited onto a glass substrate in the deposition chamber into which a reaction solution (400 mL/h) and a 5 mM H$_2$O$_2$ (oxidizing) solution (100 mL/h) were simultaneously flowed. The temperature of the deposition chamber was maintained at a constant 60°C for 8 h of deposition. Once the depositing process finished, the samples were washed with DI water several times and were then dried in an oven (100°C for 2 h), following by annealing in air in a furnace at 400°C for 5 h.

Field–emission scanning electron microscopy (FE-SEM, JEOL) and Atomic force microscopy (AFM, Bruker) were employed to examine the surface morphology of the films. Their thickness was measured by an Ellipsometer (Novanview, Korea). X-ray diffraction (XRD, Rigaku) was conducted to determine the crystal structure. The oxidation states of copper were examined using an X-ray photoelectron spectroscopy system (XPS, VG ESCA 3000). The sheet resistance–temperature dependence (R–T) of the films in a temperature range from 295 K to 368 K (22–95°C) was tested using a DSF four-point probe system
(Doosung). From the $R$–$T$ data, the TCR was calculated using a universal equation given in ref [3,24]. To determine aging characteristics, the films were aged in a tube furnace at 150°C (in air), and the room-temperature ($RT = 25^\circ C$) sheet resistance was measured at various points during aging, up to 500 h. The aging coefficient was then calculated as $\Delta R/R = (R - R_o)/R_o$ (%), where $R_o$ and $R$ are the resistance ($\Omega$) at RT before and after aging, respectively [14]. The $\rho$, TCR and $\Delta R/R$ values are the averages of five measured samples.

3. Results and discussion

3.1. Microstructure and electrical properties of Cu-doped (Ni,Mn)$_3$O$_4$ thin films

Figure 1 shows the surface morphology of the Cu-doped nickel manganite film series in the as-grown...
state, deposited at pH = 6.85. As can be clearly seen, a compact surface was achieved with a small amount of Cu (x ≤ 0.030). The films exhibited a uniform morphology with spherical grains. The grain size histograms (Figure 1f–h) established by using Image J software indicate a slight increase in average grain size (AGS) from 51.2 to 72.8 nm. In contrast, when x reached 0.035 (Figure 1d), a spread paste–like morphology appeared, and the large pores were observed. As x further increased to 0.040, the porosity became much higher, with a worse microstructure as shown in Figure 1e. To characterize the chemical composition of the films, EDS analysis was performed. Figure 1i shows the representative EDS spectrum and the detailed results are listed in the insert Table. It is found that the portion of Cu in films proportionally increased with that in the precursor solution (x).

To tailor the electrical properties of Mn3O4-based films, the composition is usually modified with some transition elements such as Ni, Co and/or Cu in the Mn matrix, which leads to a change from a single to a multi-component phase. During our practical investigation, one of the greatest difficulties when depositing thin films with multi-component compositions is that the microstructure becomes worse since the compositions contained high degrees of substitution elements. This is mainly due to the difference in the liquid–solid phase transformation characteristic of constituting elements [27]. Obviously, it is a challenge in controlling the compositions of the films, while simultaneously satisfying the requirement of dense, smooth and homogeneous bodies. Nevertheless, the measured results of electrical properties in our works [24,25] indicated that the LFD offered some promise for fabrication of highly conductive Mn3O4-based films.

Figure 2 presents the relation between RT resistivity (ρ) and Cu level (x), which was derived from the resistance–temperature (R–T) data of the Cu-doped nickel manganite film series as reported in ref [27]. It is observed that the ρ firstly decreases with x ≤ 0.025, and then increases with x ≥ 0.03. Obviously, the lowest ρ value of 200 Ω cm achieved at x = 0.025, is much lower than that of 6,300 Ω cm for the Cu-free specimen, demonstrating the strong effect of Cu on the conductivity. This confirms the results of the previous reports [9–11,15–17]. On the other hand, the absolute TCR also decreases with increasing Cu, from 3.21 to 2.38% K−1, as shown in Table 1. These results clearly imply that the conductivity was significantly induced by Cu doping, which however aggravated the sensitivity of the synthesized films. A drop in TCR with Cu doping was also reported by Cho et al. for metal–organic decomposition (MOD) nickel manganite thin films, fired at 450°C [16]. Actually, in the last ten years, various types of NTCR nickel manganite materials have been investigated including bulk, thick and thin films, which have been successfully synthesized by many different techniques. Nevertheless, to the best of our knowledge, there has been no report of an absolute TCR > 2.38% K−1, together with a ρ < 1000 Ω cm for (Mn)3O4-based ceramics produced at temperatures around 400°C. Therefore, the present electrical performance, i.e. a TCR > 2.38% K−1 and a ρ ~ 200 Ω cm, indicates the excellent benefits of Cu doping, as well as the advantage of the LFD route for synthesizing conductive Mn3O4-based thin films. These features encourage us to persist with further investigations.

A drawback, however, is revealed in Figure 2, where the ΔR/R continuously rises with Cu doping. After 500 h of aging at 150°C in air, ΔR/R was 6.8% for the Cu-free film and it rapidly increased up to 11.3% with increasing x, while it was 10.5% for the best conductive specimen (x = 0.025). These ΔR/R values are larger than those of the common nickel manganite thin films [28] and most conventional ceramics [13,15,19–21]. Obviously, the ΔR/R indicates poor electrical stability of films with Cu-rich compositions. In a very recent article, the Cu was reported to cause a remarkable resistance drift up to 33% in Ni12,Mn2–x,CuO2 ceramics upon heating at 300°C [29]. Since electrical stability is one of the crucial technical parameters for ensuring the reliability of ultimate devices, the aging characteristic is necessary to improve.

Table 1. Absolute temperature coefficient of resistance (TCR) measured at RT for the Cu-doped (Ni,Mn)3O4 thin film series annealed at 400°C, examined as a function of Cu content (x).

| x   | TCR (% K−1) |
|-----|-------------|
| 0.000| 3.21 ± 0.10 |
| 0.010| 2.93 ± 0.075 |
| 0.015| 2.89 ± 0.08 |
| 0.020| 2.73 ± 0.07 |
| 0.025| 2.52 ± 0.06 |
| 0.030| 2.38 ± 0.05 |
| 0.035| 2.41 ± 0.06 |

Figure 2. Dependence of the room–temperature resistivity and drift of sheet resistance on the Cu substitution level (x), examined on the Cu–doped (Mn,Ni)3O4 thin films [27].
3.2. Effects of further Zn doping on the characteristics of Cu–doped (Ni,Mn)3O4 thin films

To tailor the electrical stability of Cu added (Ni,Mn)3O4 thin films, the best conductive composition was selected to be further modified with Zn. The (Zn,Cu) co-doped (Ni,Mn)3O4 thin films were prepared from nickel manganese chloride solutions by simultaneously adding 0.025 mol CuCl2 and y (0.005–0.015) mol ZnCl2 under the same conditions as were used for the deposition of Cu-doped alone films, except that the solution pH was adjusted slightly lower, from 6.85 to 6.55. AFM photographs of the thin films with y = 0.000, 0.008 and 0.015 annealed at 400°C are displayed in Figure 3a–c. The comparison of surface microstructure between with (y = 0) and without (y = 0) Zn-containing specimens, indicates that both types of films have grains with a spherical morphology. However, the presence of Zn results in much finer grains. The mean grain size was evaluated by AFM histograms, and the detailed information is summarized in Table 2. It was found that the grain size decreases from 210 nm for y = 0.000 to 80 nm for y = 0.015. In general, the post-annealing process causes grain enlargement owing to the thermal kinetics. However, very little change in grain size was observed between the as–grown and heated states of Zn-rich samples. For instance, in case of y = 0.012, the grain size was found as 70 nm and 80 nm for as-grown (Figure 2d) and annealed states (Figure 2e), respectively. These results suggest that the Zn suppresses grain growth during the annealing process. Chang et al. also reported similar phenomena for ZnxFe2.5−xNi2Mn1.5O8 ceramic system, prepared by co-precipitation method [30]. The authors attributed the interaction force between the doped Zn and grain boundaries to be the main reason of this behavior, where Zn exerts a dragging effect on boundary migration during the firing step. Otherwise, it was observed that more nano-pores appear in y = 0 (Figure 3a) than in y ≠ 0 specimens (Figure 3b and Figure 3c). As Cu2+ commonly reduces to Cu+ in the solid phase under heat energy, the porosity of the Zn-free film is most likely associated with the emission of oxygen occurring during Cu2+–Cu+ conversion [31]. In contrast, since Zn2+ ions are presented in the spinel, they exclusively occupy the A–sites, which leads no (or less) vacancies available (at the A–sites) for Cu+ to reside. Therefore the valance reduction reaction of Cu is less pronounced, and thus less pores are existed in the (Zn, Cu) co-doped specimens.

The AFM line profile presented in Figure 3f shows the average roughness (Ra) of the film in Figure 3c. The Ra parameters of (Zn,Cu) co-doped film series evaluated from AFM line profiles are listed in Table 2. It is found that as y increases, Ra decreases from 89.8 to 37.7 nm. According to the above results, it is

Table 2. Grain size, roughness, and thickness of (Zn,Cu) co-doped (Ni,Mn)3O4 thin films annealed at 400°C, examined as a function of Zn content (y).

| y    | Mean grain size (nm) | Roughness (nm) | Thickness (nm) |
|------|----------------------|----------------|----------------|
| 0.000| 210 ± 10             | 89.8           | 397            |
| 0.005| 160 ± 10             | 72.5           | 376            |
| 0.008| 120 ± 10             | 60.1           | 352            |
| 0.010| 100 ± 5              | 53.1           | 339            |
| 0.012| 80 ± 5               | 41.8           | 326            |
| 0.015| 80 ± 5               | 37.7           | 308            |

Precursor solution composition (Ni2xMn3x−xCu2xZn3xCl2 with x = 0.025). Average grain size was evaluated by AFM histograms, reported in ref [32]. Roughness was calculated using an AFM scanning probe image processor (SPIP–4.8.2) program. Thickness was measured by Ellipsometer.

Figure 3. (a–c) AFM images recorded from the surface of (Zn,Cu) co-doped (Ni,Mn)3O4 thin films with y = 0.000, 0.008 and 0.015, respectively, annealed at 400°C for 5 h. Highly magnified FE-SEM images observed from the surface of the specimen with y = 0.012: (d) as–grown and (e) annealed states. (f) AFM line profile taken across the film surface in Fig. 3c.
reasonable to conclude that the addition of Zn induces a reduction in grain size and porosity, and thus leads the film surface to be smoother. These changes in microstructure characteristics will affect the electrical properties of the final products.

Figure 4a illustrates the principle of Ellipsometer measurement, where the thickness was determined by the height of the film body (distance between the surface and substrate). The insert in Figure 4a shows a representative Ellipsometer line profile, from which the thickness was derived and summarized in Table 2. To confirm the accuracy of the Ellipsometer measurement, a cross-sectional FE-SEM image was taken and compared. In this case, for the $y = 0.012$ film, the thickness evaluated from the FE-SEM image (Figure 4b) is approximately 320 nm while it was 326 nm when measured using the Ellipsometer (Table 2), which represents a very small difference in output data between these two measurement methods. For the (Zn,Cu) co-doped film series, the thickness decreased from 397 to 308 nm with $y$ within the studied range (Table 2). Obviously, the decrease in the thickness of films is basically due to the presence of Zn$^{2+}$ in the solution. Otherwise, we suggest that the change in pH of the solution should be also taken into account for this behavior. As mentioned above, the pH

![Figure 4. (a) Illustration of thickness measurement of annealed (Zn,Cu) co–doped (Ni,Mn)3O4 thin films using an Ellipsometer. The insert (lower right side) shows the line profile for the sample with $y = 0.010$. (b) Cross-sectional SEM micrograph of the film with $y = 0.010$. (c) XRD patterns of the studied films, examined as a function of Zn content ($y$).](image-url)
of the solution was slightly reduced to prevent the precipitation from occurring in the deposition chamber during the experiments. Therefore, we believe that both the Zn addition and pH adjustment caused a change in Gibbs free energy of the solution, which affects the nucleation rate of films on the substrates, and thus the film thickness.

The greatest benefit of the LFD technique in synthesizing thin films with Mn$_3$O$_4$-based compositions, is the critical temperature required to crystallize the materials can be as low as around 300°C. The crystallization mechanism of LFD films at relative low temperatures has been discussed in our earlier publication [32]. In the present work, the crystal structure of the annealed (Zn,Cu) co-doped films was analyzed using XRD, and the results are given in Figure 4c (black–solid lines). As expected, both the Zn-free ($y = 0$) and Zn added ($y \neq 0$) films were well–crystallized after annealing at 400°C in air. A cubic spinel structure (Fd–3 m space group) was revealed for all films (refers to JCPDS card No. 84–0542) without any secondary phase. The intensity of the preferential orientation (311) peak seems basically unchanged, indicating the phase structure of the films is relative stable regardless the Zn content. This is in accordance with the XRD result reported for conventional ceramics [21,30] but disagrees with the case of spin–sprayed nickel manganite thin films, where the Zn doping was found to significantly enhance the crystallinity [4,33]. On the other hand, the peak of (311) becomes gradually broader for samples exhibiting higher Zn content, which further confirms the reduction of grain size shown in Figure 3. To obtain further structure information of the present thin films, Rietveld refinement analysis was performed using Materials Analysis Using Diffraction (MAUD) program. The refined patterns (green–dash dot lines) and differences between experimental and calculated data (dark yellow–solid lines) are also depicted in Figure 4c. The results of crystallographic parameters summarized in Table 3 again confirm the symmetry (cubic) and space group (Fd–3 m) of the present films. In addition, the lattice parameter ($a$) is found to decrease with the increasing Zn. As the ionic radius of the Zn$^{2+}$ cation (0.58 Å) is smaller than that of the Mn$^{2+}$ cation (0.66 Å) [21], it is reasonable to accept that this decrease in $a$ is due to the replacement of Mn$^{2+}$ ions with Zn$^{2+}$ ions at the A sites of the spinel.

As belonging to LFD thin film system, the present films exhibit a typical NTCR characteristic, similarly to those in refs [24,25,27,32]. Figure 5a presents the $\rho$ and TCR of films examined as a function of the Zn doping level, $y$. As can be clearly seen, the $y = 0$ samples possess higher $\rho$ values, up to 4,600 $\Omega$ cm, as compared to the $\rho = 200$ $\Omega$ cm for $y = 0$ composition. However, only in Zn-rich samples ($y > 0.010$), the $\rho$ jumps rapidly while it does not change much within the range of $y \leq 0.010$. Due to the increase of $\rho$, the TCR increases from 2.52 to 3.20% K$^{-1}$ within the studied range of $y$, demonstrating an enhancement of sensitivity with Zn doping. Specially, $\rho = 820$ $\Omega$ cm and $\text{TCR} = 2.82%$ K$^{-1}$ are simultaneously obtained for the specimen with $y = 0.010$. It is clear that the addition of a reasonable amount of Zn improves the specific TCR value without an accompanying large change in resistivity.

The Hall carrier concentration ($N$) and mobility of the Zn-containing films were determined using a Hall–effect measurement system and the results are presented in Figure 5b. It was found that $N$ systematically decreases from $7.35 \times 10^{14}$ to $1.06 \times 10^{14}$ cm$^{-3}$ with increasing $y$. Since the conduction mechanism of nickel manganite is commonly ascribed to electron hopping between Mn$^{3+}$ and Mn$^{4+}$, the reduction of $N$ should be assigned to the decrease in the Mn$^{4+}$ portion (Figure 5b) which was determined using Mn 2p$_{3/2}$ XPS analysis. In Cu–doped nickel manganite spinel, a solid-state charge transfer redox system exists that oxidizes Mn$^{3+}$ to Mn$^{4+}$ and reduces Cu$^{2+}$ to Cu$^{+}$ [34–36]. Moreover, the monovalent copper occupies the A sites, while bivalent copper occupies both A and B sites of the spinel [10,11].

The presence of Cu$^{+}$ increases the amount of cations in the A sublattices, which in turn displaces some Ni$^{2+}$ cations from A to B sites. This displacement produces Mn$^{4+}$ at B sites for charge compensation, and consequently increasing the concentration of Mn$^{4+}$ ions. Since more Mn$^{4+}$ ions are present, more Mn$^{3+}$/Mn$^{4+}$ couples are available for electron hopping at the B sites, which is responsible for the large carrier concentration in the Zn-free specimen in Figure 5b, as well as the high electrical conductivity of the Cu–only doped film series in Figure 2. However, when Zn was added along with Cu to the composition, the Zn$^{2+}$ ions are exclusively located at A sites [17,37]. Thus, the Cu cations are expelled from the A sites and move into B sites. This migration causes Cu$^{1+}$–Cu$^{2+}$ conversion, and consequently, the Cu$^{+}$ ions at the A sites decrease as shown in the insert of Figure 5b. Further, as Cu$^{+}$

Table 3. Crystal data obtained from the Rietveld analysis.

| $y$   | 0.000 | 0.005 | 0.008 | 0.012 | 0.015 |
|-------|-------|-------|-------|-------|-------|
| Crystal system | Cubic | Cubic | Cubic | Cubic | Cubic |
| Space group | Fd-3 m | Fd-3 m | Fd-3 m | Fd-3 m | Fd-3 m |
| Lattice constant, $a$ (Å) | 8.279488 | 8.263745 | 8.256182 | 8.2546015 | 8.246381 |
transforms to Cu$^{2+}$, the Mn$^{4+}$ also converts to Mn$^{3+}$ to maintain the overall electrical neutrality of the lattice [21], resulting in a decrease in the Mn$^{4+}$ concentration in the present (Zn,Cu) co-doped films, as shown in Figure 5b. On the other hand, Figure 5b also reveals a decrease in $\mu$ from 20.4 to 6.4 cm$^2$/V·s with respect to the added Zn. This is most likely due to the reduced grain size of the Zn added samples, as shown in Figure 3. The small grain size induces a large number of insulating grain boundaries, consequently resulting in high-energy barriers for electron conduction [38]. As the relation of $\rho$ with $N$ and $\mu$ is expressed by $\rho = 1/Ne\mu$ ($e$ is the electronic charge) [39], the tendency of $\rho$ to decrease in Figure 5a therefore, should be attributed to the decrease in both $N$ and $\mu$ in Figure 5b.

Figure 6a shows the resistance drift ($\Delta R/R$) for (Zn, Cu) co-doped (Ni,Mn)$_2$O$_4$ films, aged at 150°C in air for 500 h. Unlike the $\rho$ tendency, the $\Delta R/R$ firstly shows a rapid decrease when $y$ varies in the range of 0.000–0.008. After that the decreasing trend continues but tends to slow down for compositions with higher Zn level. Obviously, the reduction of $\Delta R/R$ from 10.5% to 4.6% implies the strong effectiveness of Zn doping on the aging behavior of the studied films. Notably, Figure 6a shows an $\Delta R/R = 5.2\%$ for a film with $y = 0.010$. Combined with its $\rho$ (820 $\Omega$ cm) and TCR (2.82 K$^{-1}$), this film highly demonstrates a potential for the use as an NTCR detecting element. To show more information about the electrical stability, its detailed aging history is also provided in Figure 6b. It is seen that the film undergoes a sudden drift in resistance (from 0% to 4.2%) in the first 82 h of aging. After that the increasing tendency of resistance slows down and reaches a nearly saturated state after 220 h, with an $\Delta R/R$ of 5.0%. After that, only a small increase in $\Delta R/R$ can be observed during the aging duration up to 500 h. The overall resistance drift is 5.2%.

To examine the effect of ceramic oxidation on the aging phenomena, nitrogen gas with high purity (99.999%) was applied to age the films (in a tube furnace) under the same experimental conditions. The results in Figure 6a show that $\Delta R/R$ varies in a range of 2.1–3.2%. Obviously, there is a remarkable decrease in aging coefficient for those exposed in nitrogen, compared to the specimens aged in air atmosphere. These results confirm that the aging behavior...
originated from the oxidation during aging at 150°C. A similar phenomenon has been reported for Mn$_{2.34}$Ni$_{0.66}$Zn$_4$O$_7$ ceramics [19]. Therefore, to improve the stability of thin films, it is necessary to inhibit the oxidation reactions by adding Zn to the spinel.

The mechanism underlying the drift in resistance is commonly interpreted in terms of cationic oxidation and cationic migration in the spinel structure [13,18]. In the Cu–containing nickel manganite, the Cu$^+$ ions at the A sites are oxidized to Cu$^{2+}$ under aging conditions (heating in air atmosphere), which consequently causes the Cu ions to migrate to B sites from A sites [40]. This migration relates to a decrease in Cu cations at the A sites. In this work, the oxidation states of Cu before and after aging were examined on the Zn-free (y = 0) and Zn added (y = 0.010) specimens by XPS Cu2p$_{3/2}$ analysis, as presented in Figure 7. The order of binding energies (BE) in the Cu2p$_{3/2}$ region is Cu$^+$ (A) < Cu$^{2+}$ (B) < Cu$^{2+}$ (A) [10,41], and the detail Cu2p$_{3/2}$ characteristics are listed in Table 4. For Zn-free composition, the Cu2p$_{3/2}$ result in Figure 7a1–2 distinctly confirms that aging caused a decrease in Cu$^+$ concentration at A sites (Cu$^+$ (A)) and an increase in Cu$^{2+}$ ion concentration at B sites (Cu$^{2+}$ (B)) (see also Table 4).

These changes in Cu cations are in agreement with the previous results, reported for Cu–doped nickel manganite materials [15–17]. Whereas in y = 0.010 specimen, neither the Cu$^+$ (A) nor Cu$^{2+}$ (B) changed much after the aging as shown in Figures 7b1–2. In addition, Table 4 indicates that the Cu$^+$ (A) in the pristine state (before aging) of Zn–added composition is relative lower as compared to that of the Zn-free. The smaller variation in the amounts of Cu$^+$ (A) and Cu$^{2+}$ (B) ions, as well as the low Cu$^+$ (A) concentration in the pristine state can be attributed to the Zn$^{2+}$ ions which almost exclusively occupy the A sites. As a result, the Cu ions with a valence of only 2+ predominantly reside at the B sites. Accordingly, the migration of Cu ions from A to B sites becomes less pronounced, which possibly explains the relatively lower resistance drift of the (Zn, Cu) co-doped films. On the other hand, the smooth surface with fewer pores shown in Figure 3 may be an additional cause for this high stability, which possibly reduce the adsorption of oxygen, and thus hinders the oxidation of Cu$^+$ ions during aging.

It should be noted that the aging performance of the (Zn,Cu) co-doped films in this study, which attained a resistance drift as low as 4.6%, was lower than that of the undoped nickel manganite films (6.5%), prepared by spin–spraying method and annealed at the same temperature (400°C) in Ar [28]. Nonetheless, the present ΔR/R values were still higher than those of 1.7–5.2% for the Mn–Co–Ni–O thin films annealed at 650–800°C [42]. In order to confirm the reproducibility, we again produced three individual precursor solutions with x = 0.025 and y = 0.010. The deposition was divided into three batches corresponding to the three individual prepared solutions, under the same experimental conditions. Two random samples from each batch were selected to measure ρ, TCR and ΔR/R. The results summarized in Table 5 indicate high reproducibility with ρ < 1 kΩ cm, TCR 2.77%/K and ΔR/R ≤ 5.7% for the films with the composition of interest.

In this work, only a small amount of Zn was added to the solutions, so the large decrease in aging coefficient (from 10.5% to 4.6%) of the final products surprised us. We therefore examined the mass fraction of Zn and Cu in solid specimens versus y (Zn in solution) by using the inductively coupled plasma (ICP) technique, and the results are presented in Figure 8a. It is seen that the portion of Zn in solid films is much higher than those in the corresponding solutions, and reveals an increasing tendency with y. Moreover, the samples with y = 0.012 and 0.015 possessed Zn contents (4.3% and 4.6%, respectively), which are even higher than that of Cu (≤3.9%), despite the Cu molar ratio in the solutions was higher (x = 0.025). These results indicate that the Zn rather than Cu, can easily replace Mn under the present conditions. This behavior can be understood by examining the liquid–solid phase transformation.
characteristic, presented in the concentration–pH diagram in Figure 8b. As discussed earlier [27], for the films grown using the Mn$^{2+}$ matrix via LFD, the concentration–pH curve of the substituting cations determines the potential of their incorporation. In particular, the pH gap between these cations (Mn$^{3+}$ and the incorporated cation) should be as narrow as possible, in order to form the films. In Figure 8b, only a small pH gap exists between Zn$^{2+}$ and Mn$^{2+}$ along their concentration–pH curves, while a much larger one is evident between Cu$^{2+}$ and Mn$^{2+}$, especially at high Cu$^{2+}$ concentration. With such a large pH gap, incorporating Cu$^{2+}$ into the Mn$^{2+}$–based phase is relatively more difficult, compared to Zn$^{2+}$. We therefore suggest that the poor morphology of the samples doped only with Cu (Figure 1), and the relative low Cu mass portion in Figure 8a, should be attributed to the difference in the concentration–pH characteristic of Mn$^{2+}$ and Cu$^{2+}$. Whereas the similar liquid–solid phase transformation behavior of Zn$^{2+}$ and Mn$^{2+}$ is responsible for the high adhesion rate.

Figure 7. XPS spectra in the Cu2p3/2 core level of (a1–2) Zn-free and (b1–2) 0.010 mol Zn-added samples, examined before (top) and after (bottom) aging at 150°C in air for 500 h.

Table 4. Characteristics of the XPS Cu2p3/2 spectra of Zn-free ($y = 0.000$) and Zn-added ($y = 0.010$) thin films.

| Samples  | Binding energy (eV) | Peak intensity (area, %) |
|----------|---------------------|--------------------------|
|          | Cu$^+$ (A) | Cu$^{2+}$ (B) | Cu$^+$ (A) | Cu$^{2+}$ (B) | Cu$^{2+}$ (A) |
| $y = 0.000^*$ | 931.1 | 933.0 | 934.4 | 37.1 | 34.0 | 28.9 |
| $y = 0.000^*$ | 931.1 | 934.0 | 934.3 | 20.8 | 42.5 | 36.7 |
| $y = 0.010^*$ | 931.1 | 933.9 | 934.9 | 25.2 | 31.7 | 43.1 |
| $y = 0.010^*$ | 931.0 | 933.5 | 934.5 | 22.2 | 33.2 | 44.6 |

*Before aging. *After aging at 150°C in air for 500 h. A and B refer to tetrahedral and octahedral sites, respectively.

Table 5. Reproducibility of $\rho$, TCR and $\Delta R/R$ for the thin films deposited from ($\text{Ni}_{0.3}\text{Mn}_{2-x-y}\text{Cu}_x\text{Zn}_y$)$_2\text{Cl}_2$ solutions with $x = 0.025$ and $y = 0.010$, annealed at 400°C for 5 h in air.

| Properties   | Batch 1 | Batch 2 | Batch 3 |
|--------------|---------|---------|---------|
|              | SP1     | SP2     | SP1     | SP2     | SP1     | SP2     |
| $\rho$ (Ω cm) | 830     | 750     | 800     | 890     | 840     | 910     |
| TCR (%/K$^{-1}$) | 2.78    | 2.77    | 2.77    | 2.83    | 2.81    | 2.85    |
| $\Delta R/R$ (%) | 5.6     | 5.1     | 4.8     | 5.7     | 4.7     | 5.4     |

SP: sample.
from solution to the substrates that resulted in a large amount of Zn in the solid (Zn,Cu) co-doped films. Such a high Zn fraction, up to 4.68% (Figure 8a) thus significantly affects the morphology and grain size, as well as the electrical properties of the final thin films.

4. Conclusion
To fabricate high–performance negative temperature coefficient of resistance (NTCR) IR sensing materials, thin films were prepared on commercial glass substrates from (Ni_{0.2}Mn_{2.8–x}Cu_{x})Cl_2 (0.010 ≤ x ≤ 0.040) solutions, using the liquid flow deposition (LFD) method. A smooth surface with a spherical morphology was achieved for films when x ≤ 0.030, while a worse microstructure with high porosity was obtained in Cu-rich films (x ≥ 0.035). The films were annealed at 400°C, and the electrical resistivity–temperature (ρ–T) dependence was examined. It was found that the Cu doping is quite effective for reducing the electrical resistivity (ρ), but simultaneously causes a decrease in TCR and an increase in ΔR/R. However, by adding Zn along with Cu to the spinel structure, the TCR was improved without a significant increase in ρ. Notably, with the co-
doping of 0.010 mol Zn and 0.025 mol Cu, the specimens possessed a TCR = 2.82% K⁻¹ and a ρ = 820 Ω cm. More importantly, compared to Zn-free films, the (Zn, Cu) co-doped films showed a much improved electrical stability, with ΔR/R as low as 4.6%, upon aging at 150°C in air for 500 h. The results suggest that the LFD (Zn,Cu) co-doped films thin films are potential candidates for IR sensing application such as microbolometers.

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Disclosure statement

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