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Characterization of Cu-doped (Ni,Mn)₃O₄ thin films annealed at low temperatures

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ABSTRACT

Negative-temperature coefficient of resistance (NTCR) thin films were prepared from (Ni_{0.2}Mn_{2.8-x}Cu_x)Cl₂ (0.010 ≤ *x* ≤ 0.040) solutions by liquid flow deposition (LFD) method. Influence of the Cu on the structural and electrical properties of the films annealed at 400°C was studied. It was found that the incorporation of copper (Cu) promoted an increase in both the crystallinity and grain size of the films. As Cu level increased, the absolute negative temperature coefficient of resistance (*TCR*) of the films was slightly decreased from 3.21% to 2.38%K⁻¹. On the other hand, the electrical resistivity (*ρ*) of the films significantly dropped with an increase of Cu, which was attributed to the improved carrier concentration rather than the enlarged grain size. The best electrical performance with *ρ* ~ 200 Ωcm was achieved in the film with *x* = 0.025 at room temperature. We provide the discussion on the conduction mechanism, particularly, for the high conduction behavior of the films via the changes of oxidation states of the manganese.

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Liquid flow deposition; thin films; spinels; nickel-copper-manganite; solution process; IR sensors

1. Introduction

Recently, there is a growing interest in microbolometers (uncooled infrared (IR) detectors) due to their advantages of various optional design, less power consumption and cost effectiveness [1–3]. For achieving high sensitivity, detecting materials with a high temperature coefficient of resistance (*TCR*) and a modest resistivity (*ρ*) are integrated into these devices [1,3–5]. In practical, the use of thin films as the detecting element resulted in much faster responding signals for devices, compared with those of bulk and thick film counterparts [4,5].

Vanadium oxide (VO_x) is one of the most commonly used materials as the detecting element for microbolometers owing to its high *TCR* of about 2 ~ 3%K⁻¹ and low synthesis temperatures [6]. Its fabrication, however, relied heavily on the contamination-free procedures in the complementary metal oxide semiconductor (CMOS) line, facing the challenges such as requirement of high cost equipment, the reproducibility issue, and the difficulties in controlling the stoichiometric compositions and electrical properties. In addition, due to its non-crystalline structure, the VO_x usually exhibited the large noise (1/*f*). Some other materials which possessed high *TCR* such as amorphous silicon [7], amorphous silicon carbide [8], and polycrystalline silicon-germanium [9] were also investigated; the large noise was still unavoidable drawbacks that impeded their uses in the aforementioned purpose.

Recently, the nickel-manganite (NiMn₂O₄) has been proposed to be a promising candidate for IR sensing applications, due to its electrical resistance that decreased precipitously with increasing temperature [1,10–12]. This material system possessed the spinel-type structure with the general formula AB₂O₄ (A: tetrahedral, and B: octahedral sites). Its semiconducting properties were typically interpreted in terms of the electron hopping conduction between Mn³⁺ and Mn⁴⁺ states at octahedral sites [4,5,10]. It was found that in the nickel-manganite compounds, the substitution of manganese by some appropriate transition metal ions (suitable for tetrahedral A sites occupation) allowed the Ni²⁺ to occupy octahedral (B) sites, leading to an improved electrical conductivity [11,13]. Among the available transition metals, copper (Cu) was reported as the most effective ion on improved conductive properties, without a significant degradation of *TCR* [14].

In the last ten years, many nickel-manganite thin films with high electrical performances were synthesized. For example, an electrical resistivity (*ρ*) as low as 250 Ωcm and a high absolute *TCR* of ~3.9%K⁻¹, were achieved for thin films with Mn-Co-Ni-O oxide composition, by sputtering method [15]. Hou et al. also demonstrated the chemical solution deposited films with a *TCR* of up to 4.12%K⁻¹ [4]. More recently, Jeon et al. reported an excellent electrical behavior of the Mn-Cu-Ni-O films with *ρ* ~ 30.9 Ωcm and *TCR* ~ 3.2%K⁻¹, prepared by metal-organic decomposition [16]. The

electrical properties of these investigated films were even much better than those of the VO_x [6]. Obviously, the progress in synthesis has led to improved quality of the nickel-manganite system with high TCR and low resistivity. However, there have been still a couple of challenges encountered for practical uses of the thin films in microbolometer devices. One of these is the high synthesis temperature. In most relevant literatures, the crystallized films were only obtained at annealing temperatures above 500°C [1,17], which deteriorated the compatibility with the current CMOS technology where the typical processing temperatures should be less than 400°C [14].

Among several routes proposed for the synthesis of nickel-manganite thin films at low temperatures, the liquid flow deposition (LFD) has been known as solution-based process, taking the advantages of non-vacuum, low-energy consumption, environmental friendliness, cost effectiveness and the capability of using various types of substrates [18]. In the previous publication [19], we demonstrated the synthesis of tetragonal nickel-manganite spinels by LFD from Ni^{2+} and Mn^{2+} cations with a chloride solution. This technique was then extended for fabricating $(\text{Ni},\text{Co},\text{Mn})_3\text{O}_4$ cubic spinel-type oxide, yielding highly conductive thin films at a modest annealing temperature of 400°C [20]. The advantage arose the fact that the LFD allowed the Mn^{3+} cations to be easily formed (from Mn^{2+}) in the liquid solution, before being absorbed into the films during deposition. As the Mn^{3+} cations were preexisted in the as-prepared state, the required thermal energy for the film crystallization was low, thus decreasing the annealing temperature. This enabled us to see a possibility of preparing $(\text{Ni},\text{Cu},\text{Mn})_3\text{O}_4$ thin films using the abovementioned procedure. Furthermore, as Cu was used to substitute, in part, for the manganese (Mn) in the $(\text{Ni},\text{Mn})_3\text{O}_4$ compound, therefore expecting the excellent conductivity. We thus prepared the films from aqueous solution with nominal composition $(\text{Ni}_{0.2}\text{Mn}_{2.8-x}\text{Cu}_x)\text{Cl}_2$ ($x = 0.010 \sim 0.040$). Particularly, we focused on the effect of Cu on the structure, microstructure and electrical property of films, annealed at 400°C .

2. Experimental procedure

2.1. Precursor solution preparation

The growth of thin films onto Si substrates has been carried out in the liquid phase via the chemical equilibrium between the metal-complexants and the metal oxides [13,21]. In order to determine the possibility of replacing manganese by copper, we examine pH-dependent concentration via a series of experimental precipitate observations from chloride solutions at 60°C . In particular, ammonia was added gradually to a solution to increase the pH to where the bulk

precipitates could be observed, so-called “precipitation point” (PP). A liquid-precipitate transformation curve was then established by connecting the PPs where the pH induced precipitation in solutions, as shown in Figure 1(a). For a given ion, for instance Ni^{2+} as shown in Figure 1(a), the liquid and solid precipitate regions were clearly separated by the curve, indicating the liquid-solid phase transformation. In a similar way, the plots for the four cations: Mn^{2+} , Ni^{2+} , Co^{2+} and Cu^{2+} were made in the same coordinate axes, as shown in Figure 1(b). A couple of points should be noted, based on our experimental observations. First, the films were formed only via the ion-by-ion mechanism [22], which was associated with the heterogeneous nucleation process; whereas homogeneous nucleation usually produced the bulk precipitates in solution, which degraded the surface quality of the films. Second, for the films grown using the Mn^{2+} matrix, the pH gap between Mn^{2+} and another cation, dominated the possibility of their incorporation: the smaller the pH gap was, the easier it was for film formation. Due to the similar concentration-pH characteristics of the three cations, i.e., Mn^{2+} , Ni^{2+} and Co^{2+} , as shown in Figure 1(b), the cobalt (II) ions were chosen to modify the $(\text{Ni},\text{Mn})_3\text{O}_4$ compound in our previous work [20]. In contrast, the large pH gap evident between Cu^{2+} and Mn^{2+} , implied that the substitution of Mn^{2+} by Cu^{2+} is relatively more difficult than by Ni^{2+} and/or Co^{2+} . Nevertheless, the region in Figure 1(b) marked by the pink-dashed rectangle, at the concentration of $<12\text{ mM}$ of Cu^{2+} , in which the PPs became much closer to each other, demonstrated a possibility of modifying manganese with only a small amount of copper.

We used $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (99.999%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (99.999%) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (99.999%) (purchased from Sigma-Aldrich) as raw materials for preparing the reaction solutions with the following compositions: $(\text{Ni}_{0.2}\text{Mn}_{2.8-x}\text{Cu}_x)\text{Cl}_2$ with $x = 0.010, 0.015, 0.020, 0.025, 0.030, 0.035$ and 0.040 . Deionized (DI) water was used as a solvent to dissolve these compounds to form solutions with a concentration of 50 mM . During the solutions being continuously stirred, an appropriate amount of NH_4Cl was added and mixed. The resultant solutions were used as the precursors for thin film deposition after 1 h stirring.

2.2. Thin film deposition

Our earlier report described in detail the experimental process of thin film deposition via LFD [19]. In this work, we adjusted the pH in a range of $6.65 \sim 6.85$ by adding ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$) to prevent precipitation. The reactant and oxidizing solutions (H_2O_2 , 5 mM) were flowed simultaneously into the deposition chamber, where a Si/SiN_x wafer ($2.5 \times 2.5\text{ cm}^2$) was, at the rates of 400 and 100 ml/h , respectively. The substrate temperature was kept constant at 60°C during the

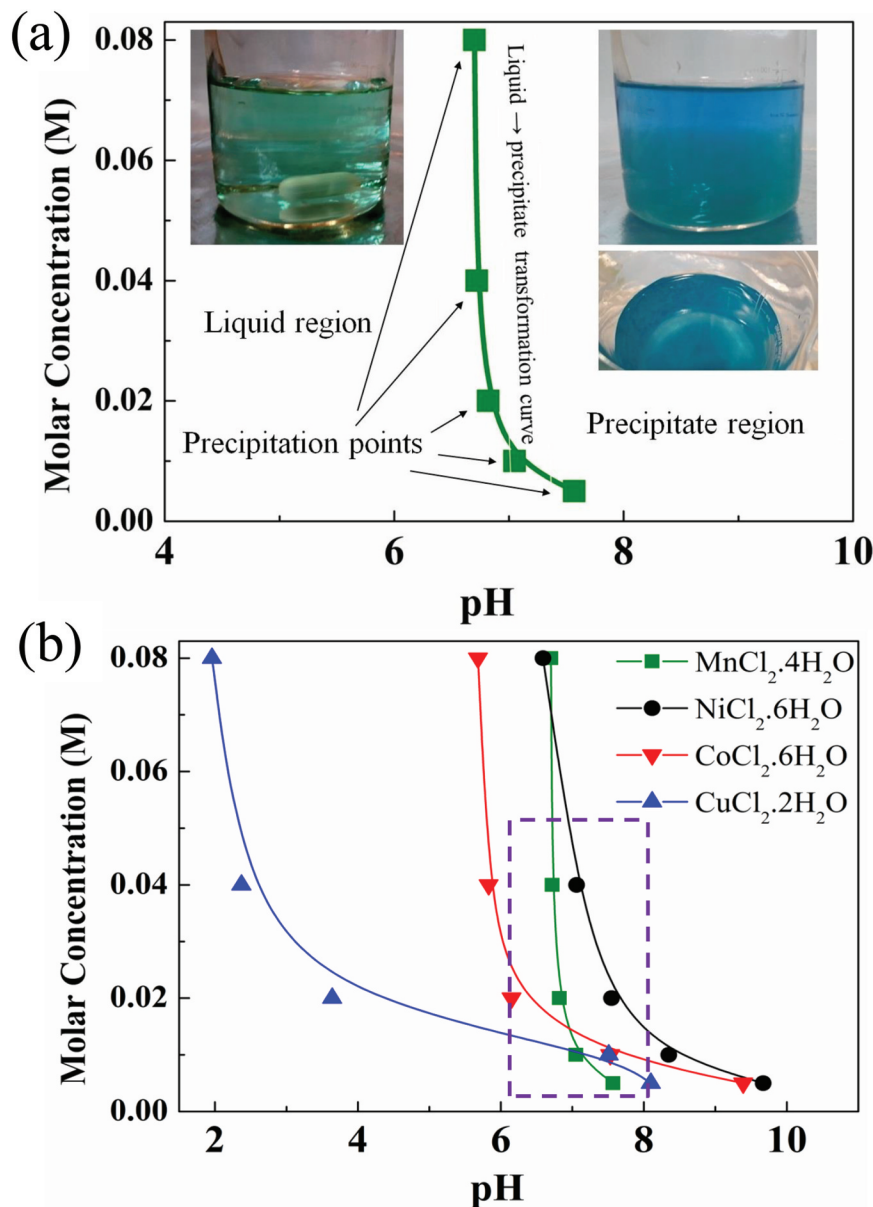


Figure 1. (a) Concentration vs pH diagram plotted based on experimental data shows liquid → precipitate transformation curve of Ni. Insert: 0.04 M absolute aqueous solution with green color of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (left) dissolved in D.I water without adding any $\text{NH}_3 \cdot \text{H}_2\text{O}$. The color of solution changed due to the precipitate formation (right) in solution when pH reaches to 6.72. (b) Concentration versus pH diagram for Mn, Ni, Co and Cu. Pink rectangular points out a possible region for depositing films with a ternary Cu-Ni-Mn oxide composition in this work.

whole deposition. The growing time was set as 8 h for each sample. After deposition, the films were washed by DI water and were then dried at 100°C for 2 h in an oven. Finally, all the specimens were annealed at 400°C for 5 h in air (with the heating rate of 5°C/min) to form crystallized films.

2.3. Characterizations

An atomic force microscope (AFM, Neos, Bruker, Germany) and a field-emission scanning electron microscope (FE-SEM, JEOL, Japan) was used to examine the surface morphology of the films. The structure of the products was further investigated by transmission electron microscopy (TEM, JEM

2100, JEOL, Japan). For TEM analysis, the film body was mechanically peeled off from the Si substrate, and then was ultrasonically dispersed in isopropanol for 2 h. The resulting solution was dropped onto a carbon-coated Cu grid and then dried. Finally, a material piece with the size larger than 5 μm was selected for examination. An X-ray diffractometer (XRD, Rigaku, Japan) was applied to examine the crystal structure. The oxidation states of manganese were examined by an X-ray photoelectron spectroscopy (XPS) system (VG ESCA 3000, Microtech, UK). A Hall effect measurement system (HMS-3000) was used to investigate the carrier concentration and mobility. The sheet resistance-temperature dependence (R - T) of the films in

a temperature range from 22°C to 95°C was measured using a four point probe system (VP75, DSF system, Doosung, Korea) which was composed of a probe station, a purpose-built automated data acquisition system and a computer-controlled electrical source meter. To examine the stability, the films were aged in an oven at 150°C (in air), and the room-temperature (RT) sheet resistance was measured at various points during aging, up to 500 h. The aging coefficient was defined as $\Delta R/R_0 = (R - R_0)/R_0$ (%), in which R_0 and R are the resistance at RT before and after aging, respectively.

3. Results and discussion

3.1. Surface morphology of the as-grown films

Figure 2 shows the surface morphology of the films at as-grown state. It was found that with $x \leq 0.025$, a compact surface was achieved for

all as-grown films as presented in Figure 2(a–e). A spherical bead-like architecture could be clearly seen with no contamination throughout the surface area. The films revealed reasonably smooth and uniform morphological characteristics. No significant differences in the morphology were found among these films, except for a slight difference in the grain size. The mean grain size (listed in Table 1), evaluated from the FE-SEM images by using Image J software [23], ranged from 50 to 70 nm for the film series. In contrast, the change in the surface morphology of the as-grown thin films at higher Cu levels in the precursor solution ($x \geq 0.030$) is clearly displayed in Figure 2(f–h). The film with $x = 0.030$ (Figure 2(f)) showed a fair uniformity of interconnected spherically shaped grains with approximately 40 ~ 100 nm in size. However, some large precipitated bulks existed on its surface. When

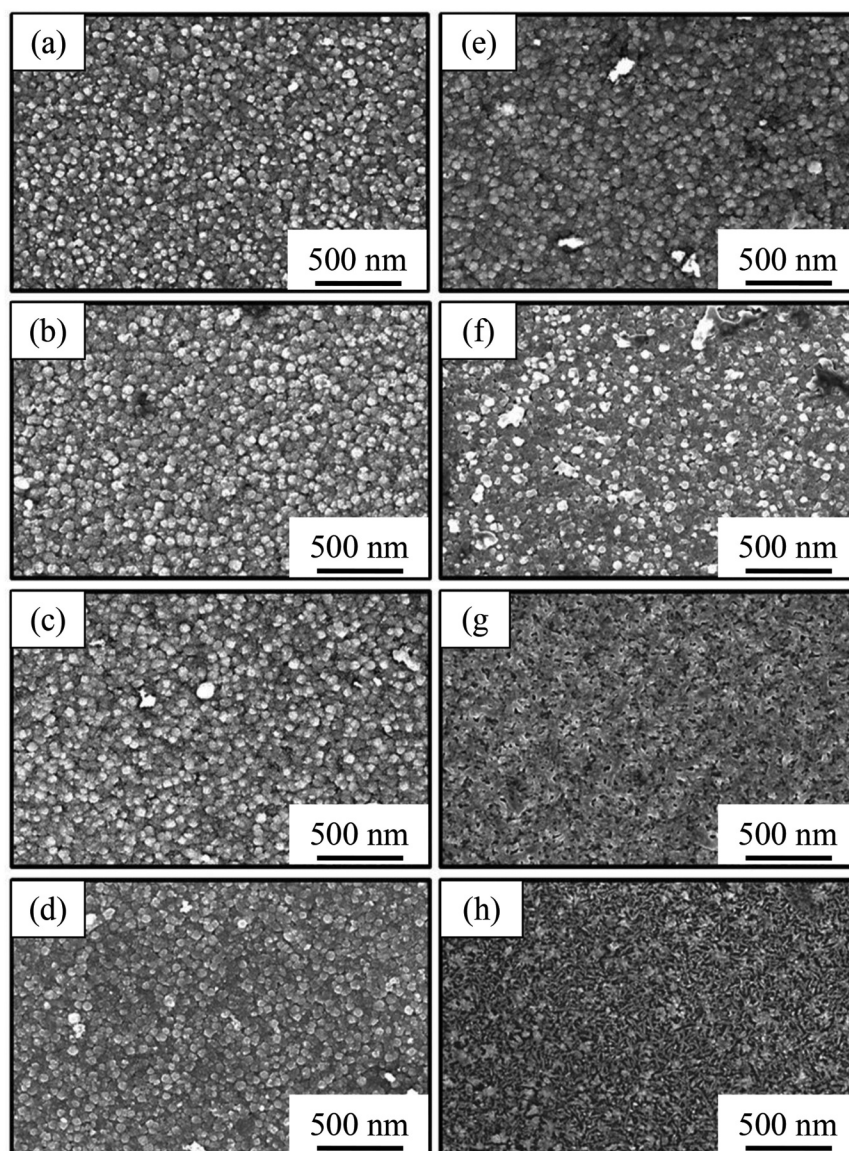


Figure 2. Surface FE-SEM micrographs of the as-grown films: (a) $x = 0.000$, (b) $x = 0.010$, (c) $x = 0.015$, (d) $x = 0.020$, (e) $x = 0.025$, (f) $x = 0.030$, (g) $x = 0.035$ and (h) $x = 0.040$.

Table 1. Chemical composition, grain size and thickness of films.

	Cu/(Mn+Ni +Cu) (mass%)	Ni/(Mn+Ni +Cu) (mass%)	Mean grain size (nm)	Mean grain size (nm)	Thickness (nm)
0.000	–	–	50	120	420 ± 10
0.010	1.59	10.2	60	150	420 ± 10
0.015	2.02	9.6	60	160	450 ± 10
0.020	2.87	11.2	60	180	450 ± 10
0.025	3.78	10.7	65	210	400 ± 10
0.030	4.13	12.1	70	220	300 ± 15
0.035	4.76	11.5	–	–	100 ± 20

Annealing temperature: 400°C

Average grain size was evaluated from surface photographic FE-SEM and AFM images by using Image J software [23].

Thickness was evaluated from cross sectional FE-SEM images

Element content was extracted from ICP-OES data.

x reached 0.035, the grains were converted into a spread paste-like morphology, being accompanied by the pores appearing on the surface as shown in Figure 2(g). As x increased to 0.040, the porosity rapidly became higher, resulting in the worse microstructure where only a poor needle like morphology was found as clearly seen in Figure 2(h).

3.2. Microstructure and crystal structure of films annealed at 400 °C

In general, the post-annealing process is required for the film crystallization as the second step of film synthesis [24], and this commonly causes the changes in grain size and surface roughness. Figure 3(a–c) shows the AFM three-dimensional (3D) topographical images of the annealed samples with different Cu contents. It was found that the annealing process induced a grain growth, as the grain size of annealed films was much larger than that of their as-grown state (Figure 2). The detailed information of the grain size of the annealed films is

listed in Table 1. In addition, Figure 3(a–c) indicates an increase in grain size with respect to the Cu adding, similar to the case of the Co-modified (Ni,Mn)₃O₄ films [20]. As the grain was enlarged, the film surface became rougher. The surface average roughness (R_a) of the films (in Figure 3(a–c)), was estimated to be 52.6, 74.7 and 89.8 nm, respectively, by using the SPIP software. On the other hand, the thickness of the film series did not substantially change as it varied within a small range of 400 ~ 450 nm (Figure 3(d, e)). However, the thickness decreased rapidly for the high Cu-containing samples when $x \geq 0.030$, as shown in Figure 3(f, g).

The crystal structure of both the as-grown and the heated films was analyzed by a XRD instrument as shown in Figure 4. The as-grown films exhibited an amorphous phase but the crystallization was found in the films after annealing at 400°C. The classical spinel (space group $Fd3m$) of the cubic symmetry could be indexed according to the major peaks, referenced to the NiMn₂O₄ with JCPDS card No. 84-0542. All peaks are clear and are in agreement with the observations for the nano-powder with the composition of Ni_{0.45}Cu_{0.55}Mn₂O₄, prepared by co-precipitation method [25]. The (311) peak possesses the highest intensity, indicating clearly the preferential orientation of the films. Moreover, the peak intensity uniformly increases with the elevation of Cu level, demonstrating an enhancement of the crystallinity with Cu in the nickel-manganite. When $x \geq 0.030$, the peaks gradually decreased in intensity, possibly due to the poor surface coverage (Figure 2(g, h)) and/or the decrease in thickness (Figure 3(f, g)). No metals or other visible impurities were observed within the XRD instrument detection limit,

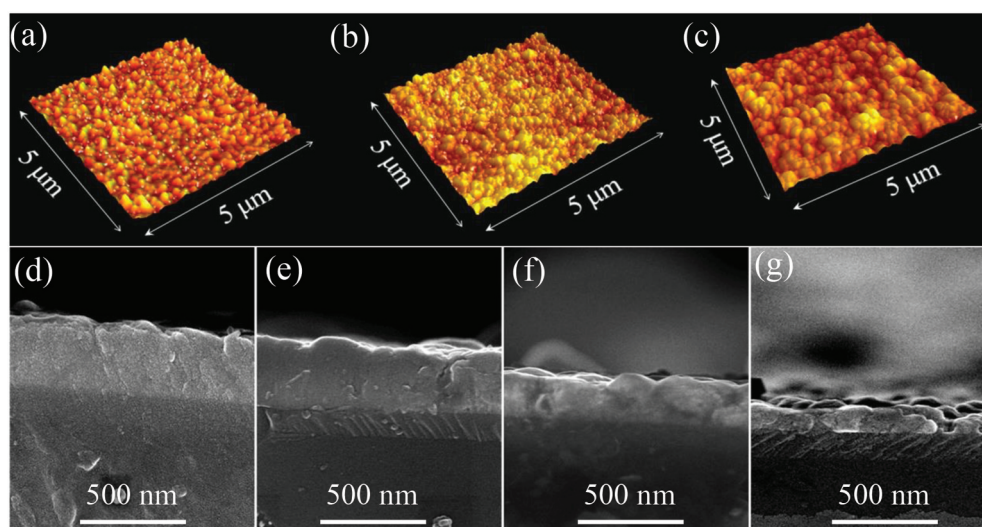


Figure 3. Three-dimensional (3D) AFM topographical images of films annealed at 400 °C: (a) $x = 0.000$, (b) $x = 0.015$ and (c) $x = 0.025$. (d–g) cross-sectional FE-SEM observations of the annealed films with $x = 0.000$, 0.020, 0.030 and 0.035, respectively.

indicating that only the single spinel phase with the prototype of AB_2O_4 transformed from the amorphous phase through heat treatment. Our previous work [19] investigated that the Cu-free composition belongs to tetragonal spinel and, thus the phase transformation from tetragonal to cubic spinel must have occurred in the range of $x = 0.000 \sim 0.010$. This point is very interesting, but was not the main focus of the present study.

According to the published phase diagram [26,27] of the $NiMn_2O_4$ system, at temperatures less than 400°C , only metastable spinel could be formed but this phase was then oxidized and decomposed irreversibly into $NiMnO_3$ and Mn_2O_3 , in the higher temperature range of $400 \sim 750^\circ\text{C}$. The stoichiometric spinel compound $NiMn_2O_4$ formed only at temperatures higher than 600°C when sintering in reducing atmosphere and, higher than 750°C in the case of air sintering. Here, the cubic spinel structure was established at temperature of 400°C , manifesting the advantage of the LFD technique as compared to most of the other synthesis routes. The formation of the spinel cubic symmetry in the studied films may be attributed to two possible reasons. First, the concentration of manganese decreased as a result of its replacement by the substituting elements (Ni and Cu). This led to the small number of Jahn-Teller active ions, with a consequence of no interactions among them in the octahedral sites [1]. This resulted in the random distribution of directions of the elongated axes, and the formation of a cubic symmetry rather than a tetragonal one. The second one was due to the preexisting Mn^{3+} ions in the as-grown state; no more oxidizing reactions of

$Mn^{2+} \rightarrow Mn^{3+}$ were needed in the solid state through annealing. Therefore, the heat treatment played a major role as a driving force only for the rearrangement of ions into the lattices for crystallization, which required a relatively low thermal energy (thus low annealing temperatures) [20].

For more information about the phase and structure of the final product, the specimen having the best crystallinity ($x = 0.025$), was selected for further TEM analysis. As mentioned above, except for the samples with Cu (x) exceeding 0.035, the studied films possessed a quasi-spherical-like morphology, including that with $x = 0.025$ (Figure 5(a)). Nevertheless, these grains actually consisted of a large amount of relatively small nanoparticles, as observed from the highly magnified FE-SEM image (inset in Figure 5(a)) taken without Pt or Au coating. The existence of these fine particles was further confirmed by TEM observation, as shown in Figure 5(b). As expected, many nanoparticles were found on the Cu grid within a grain scale, and the average size of these nanoparticles, estimated from the enlarged TEM image (Figure 5(c)), was ca. 4 nm. Figure 5(c) also revealed a single-crystalline of the nanoparticles, and the interplanar spacing of the lattice planes (d) was approximately 0.25 nm, as shown in the HRTEM image (inset in Figure 5(c)). This result was in agreement with the known value of (311) planes of $NiMn_2O_4$ ceramics [28], which further verified the excellent crystallization of the films with (311) orientation. Moreover, as having a lattice spacing (d) of nearly 0.25 nm, the present ceramic system was assigned to an intermediate spinel structure between a normal spinel structure (AB_2O_4)

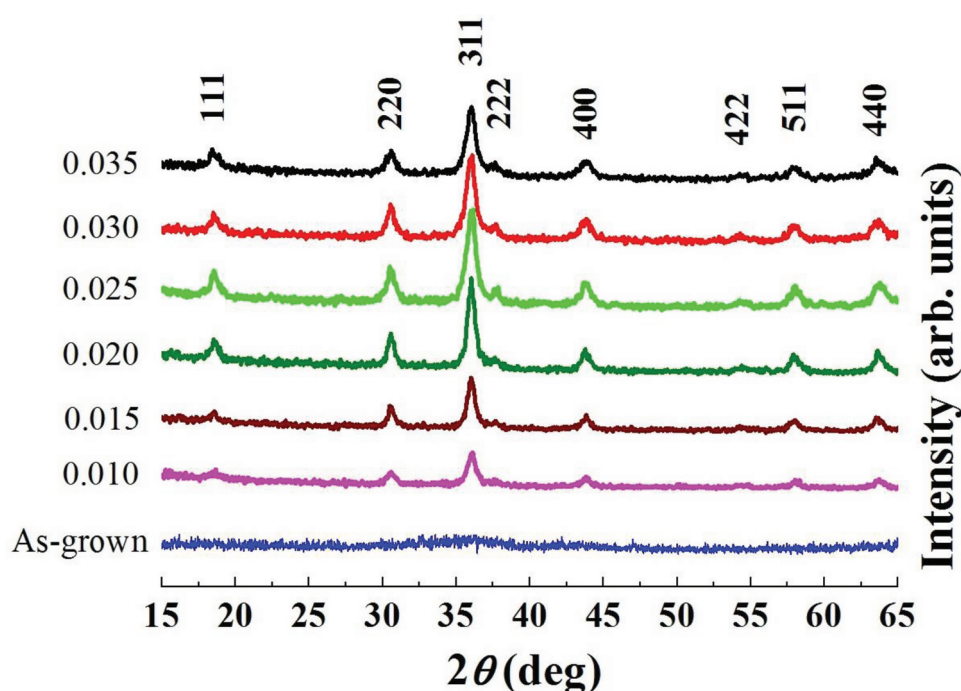


Figure 4. XRD patterns of the annealed films, examined as a function of Cu level.

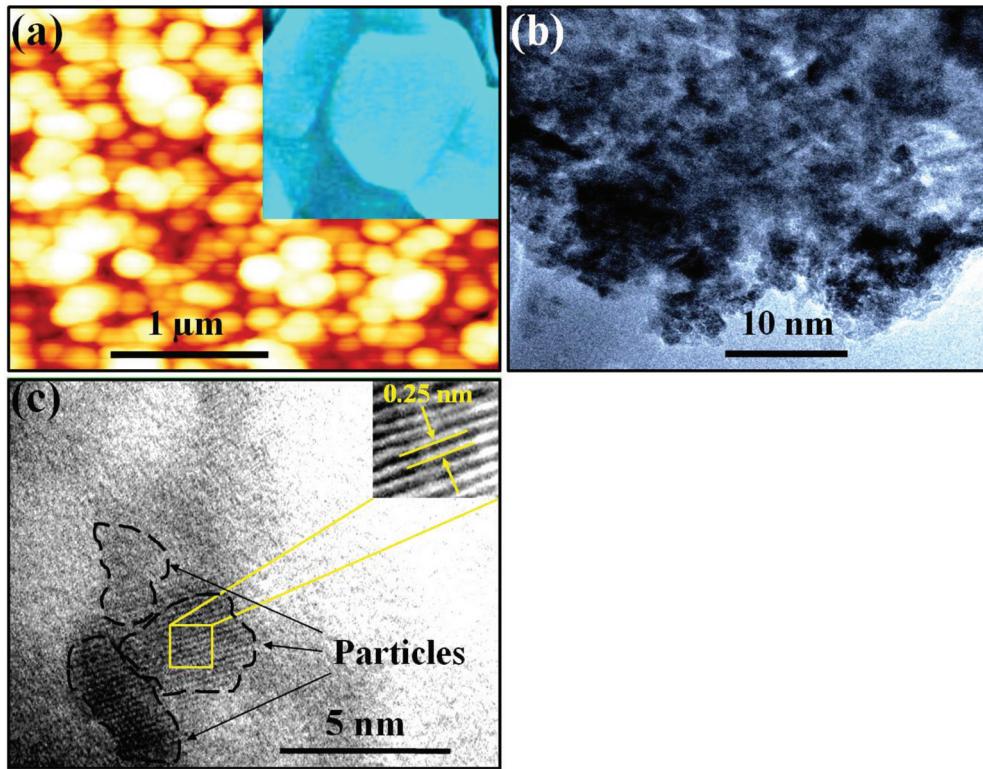


Figure 5. Structural analysis of the annealed film with $x = 0.025$: (a) AFM image, Insert: high magnified FE-SEM observation (without Pt or Au coating) shows a large amount of nanoparticles, (b) TEM image of the nanoparticles and (c) enlarge TEM image shows the nanoparticle size (marked by dash-black lines). Inset in Fig. 5(c) is the HRTEM image observed in a selected area of a single nanoparticle.

and an inverse spinel ($B[AB]O_4$) structure, rather than to a pure standard spinel ($d = 0.19$ nm, referred to JCPDS card No. 84-0542).

3.3. Electrical properties

The sheet resistance of the annealed films deposited at different Cu substitution levels was measured by the four-point probe technique. The resistivity (ρ) was then simply calculated by a universal equation [29]: $\rho = R \times t$ where ρ is the film resistivity (Ω cm), R is the sheet resistance ($\Omega/\square$), and t is the film thickness (cm).

Figure 6(a) shows the (ρ)-temperature (T) curve in a testing temperature range $T = 295$ – 368 K (22 – 95° C). The resistivity decreased with increasing T , demonstrating a typical NTCR behavior for the films. On the other hand, from the sheet resistance R - T data, the relationship between $\ln(R/T)$ and the reciprocal of the absolute temperature ($1000/T$) for film series was derived as shown in Figure 6(b). These two parameters displayed a nearly linear relationship over the measured temperature range. This linear dependence was attributed to the hopping transport mechanism whereby the R - T relationship was commonly described by the well-known expression [30,31]: $R = C \exp(E_a/k_B T)$, where C is a constant,

T is the absolute temperature, E_a is the activation energy for the electrical conduction, and k_B is the Boltzmann constant.

In practice, the temperature coefficient of resistance at room temperature (300 K), denoted by TCR_{300} , is known as the most important factor of technical interest for an NTCR detective element. The TCR_{300} value could be calculated by the following equation [4,19]:

$$TCR_{300} = \frac{1}{R_T} \frac{(R_{T1} - R_{T2})}{(T_2 - T_1)} (\%K^{-1})$$

R_{T1} , R_T and R_{T2} are the film specific resistance (Ω) at T_1 , T and T_2 (K), respectively. Here, $T = 300$ K is the measured temperature, and $T_1 = 295$ K and $T_2 = 305$ K are the chosen reference temperatures. On the other hand, although the requirements on ρ values not being so strict, the variable ρ can provide flexible options for device geometric design. In addition, a device with low noise ($1/f$) and a low power requirement can be achieved using of a detective element with a modest resistance. Therefore, materials with relatively low resistivity benefits the fabrication of small-sized microbolometer devices.

Figure 7 shows the change in ρ_{300} and absolute TCR_{300} examined as a function of the Cu substitution level, x . The ρ_{300} and TCR_{300} results were derived from the average data of sheet resistance (R), measured from three different samples at each condition. As

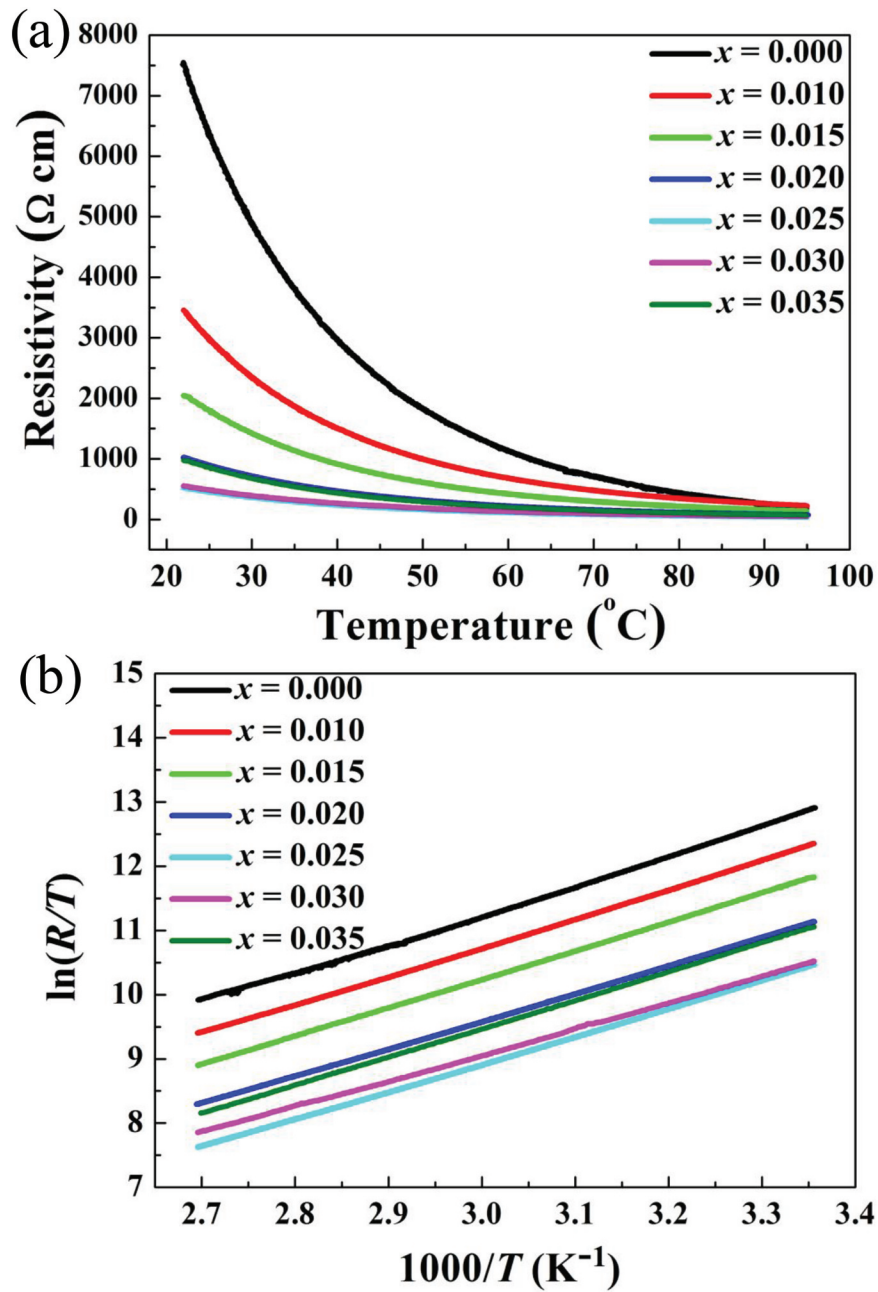


Figure 6. (a) Resistivity-temperature (ρ - T) curve and (b) plot of $\ln(R/T)$ versus $(1000/T)$ for the films.

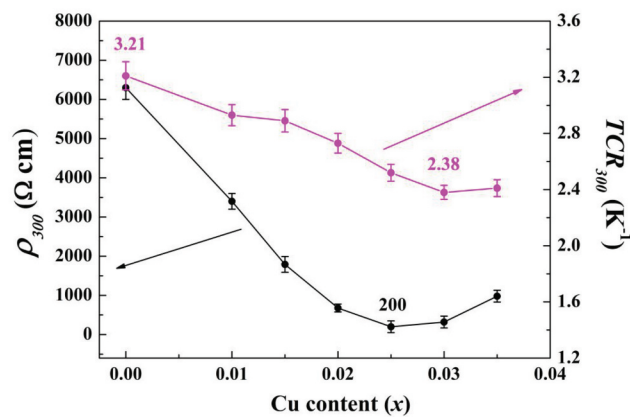


Figure 7. Dependence on the Cu substitution level of the room-temperature resistivity (ρ_{300}) and temperature coefficient of resistance (TCR_{300}) examined on the studied films.

shown in Figure 7, with increasing x within the range of $x \leq 0.025$, the ρ_{300} value decreased significantly, and then tended to increase with $x \geq 0.030$. The best value, 200 Ω cm, achieved when $x = 0.025$ was far lower than 6,300 Ω cm for the Cu-free sample, demonstrating an improved conductivity for the films. Furthermore, the specific resistivity value (200 Ω cm) corresponds to the Cu substitution of only 2.5 mol%, was much lower than those of the nickel-manganite films ($\rho > 600$ Ω cm), modified with 6.5 ~ 8.2 mol% Co, via the same route [20]. This result gave the evidence of stronger effects of the copper substitution on the conductive behavior of nickel-manganite films, when compared to that of cobalt. On the other hand, the absolute TCR_{300} also decreased with x but maintained between 2.38% and 3.21% K^{-1} . This implied the relatively high sensitivity of the specimens to the temperature. The measured TCR_{300} in this work were comparable to those of the Cu-doped nickel-manganite films produced by spin spray deposition [14], whereas the specific ρ_{300} was much lower. To the best of our knowledge, although various values of TCR have been found in bulk, thick and thin film forms, there has been no report of an absolute $TCR > 2\%K^{-1}$, together with a $\rho < 500$ Ω cm at RT, for the spinel nickel-manganite -based ceramics synthesized at the temperature domain of 400°C.

Hall-effect measurement was applied to determine the following carrier transport properties of the films: the carrier type, carrier concentration and mobility. The results of Hall-effect measurement with Van der Pauw geometry, performed at room temperature, are shown in Table 2. In general, a positive value of the charge carrier indicates p-type conduction whereas a negative value the n-type conduction [32]. In this work, the films show a negative charge value, demonstrating an unambiguous n-type nature with electrons considered as major carriers. This finding agreed with the early investigation [33,34], although the nickel-manganite ceramic sometimes being mistaken as a p-type semiconductor [35]. The relation of ρ with carrier concentration (N) and carrier mobility (μ) expressed by $\rho = 1/Ne\mu$ (e is the electronic charge) [36], indicates that both N and μ contribute to the conductivity. As shown in Table 2, N systematically increased whereas μ decreased with Cu in the films. Therefore, N rather than μ , should relate to the drop tendency of ρ_{300} in Figure 7. Otherwise, despite the decreasing trend with x , high carrier mobility of up to 29.0 cm^2/Vs would have

been demonstrated for the films, as an order of magnitude greater than that of the nickel-manganite ceramics [37]. This may explain the high conduction in the thin film forms and, thus the faster output signals of the integrated thin film devices when compared with those of their bulk counterparts.

Although the conduction mechanisms of the nickel-manganite system were still poorly understood, most researchers attributed the electrical conduction in this material to the small-polaron hopping between Mn^{3+} and Mn^{4+} states at octahedral sites [38,39]. The charge carriers (electrons) were emitted via the change in valence of Mn cations (from Mn^{3+} to Mn^{4+}). These charge carriers locally vibrated around their lattice positions, deforming the surrounding lattices and carrying these deformations along with them under the influence of external electric field. As the improvement of electrical conductivity was majorly due to the increased carrier concentration, which associated with the change of oxidation states of manganese, an extensive XPS analysis was performed to identify the manganese valences in the present $(Cu,Ni,Mn)_3O_4$ phase. The representative XPS survey scan and high resolution Mn 2p_{3/2} region are displayed in Figure 8(a, b), respectively. All the peaks in Figure 8(a) could be indexed to Mn, Ni, Cu, O, and C. In this case, the C came from a foreign hydrocarbon source of the XPS instrument itself. Figure 8(b) shows the three peaks with the binding energy (BE) ranging from 633 to 650 eV, demonstrating the co-presence of the three different manganese valences in the films. Obviously, the BE values in Figure 8(b) were consistent with those given in the literature for spinel nickel-manganite compounds [26]. For $NiMn_2O_4$ -based ceramics, the higher BE peaks at 641.2 eV and 642.0 eV in the Mn 2p_{3/2} region were attributed to Mn^{3+} and Mn^{4+} cations, respectively [40], whereas the low BE peak of 640.3 eV was to Mn^{2+} . In this work, the Mn^{2+} , Mn^{3+} and Mn^{4+} peaks were found in the Mn 2p_{3/2} region in the ranges of 636.78–637.94 eV, 640.76–641.71 eV, and 642.54–643.29 eV, respectively. In addition, the decrease in BE could be seen at Mn^{2+} and Mn^{4+} peaks, for Cu-containing compounds, as revealed by the dashed-blue lines in Figure 8(c). This shift behavior may be ascribed to a slight weakening of the Mn-O bonds in the presence of copper [41,42]. The characteristics of the peaks for the studied compositions are summarized in Table 3. As can be observed from Table 3, the obtained portions of Mn^{2+} and Mn^{3+} lie between the ranges expected for non-stoichiometric compositions. Furthermore, as more Cu ions are present, the relatively more tetravalent manganese (Mn^{4+}) cations are found in the films. The influence of Cu incorporating into the $(Ni,Mn)_3O_4$ matrix is illustrated, for instance the sample with $x = 0.035$ exhibits a much higher Mn^{4+} concentration of up to 75.79%, as compared to that of 44.12%

Table 2. Carrier concentration and carrier mobility of films.

x	Carrier concentration (cm^{-3})	Carrier Mobility ($cm^2/V.s$)
0.000	-4.44×10^{13}	29.0
0.010	-8.57×10^{13}	25.4
0.015	-1.37×10^{14}	25.5
0.020	-2.87×10^{14}	24.7
0.025	-7.35×10^{14}	20.4
0.030	-8.79×10^{14}	16.0
0.035	-1.79×10^{15}	4.40

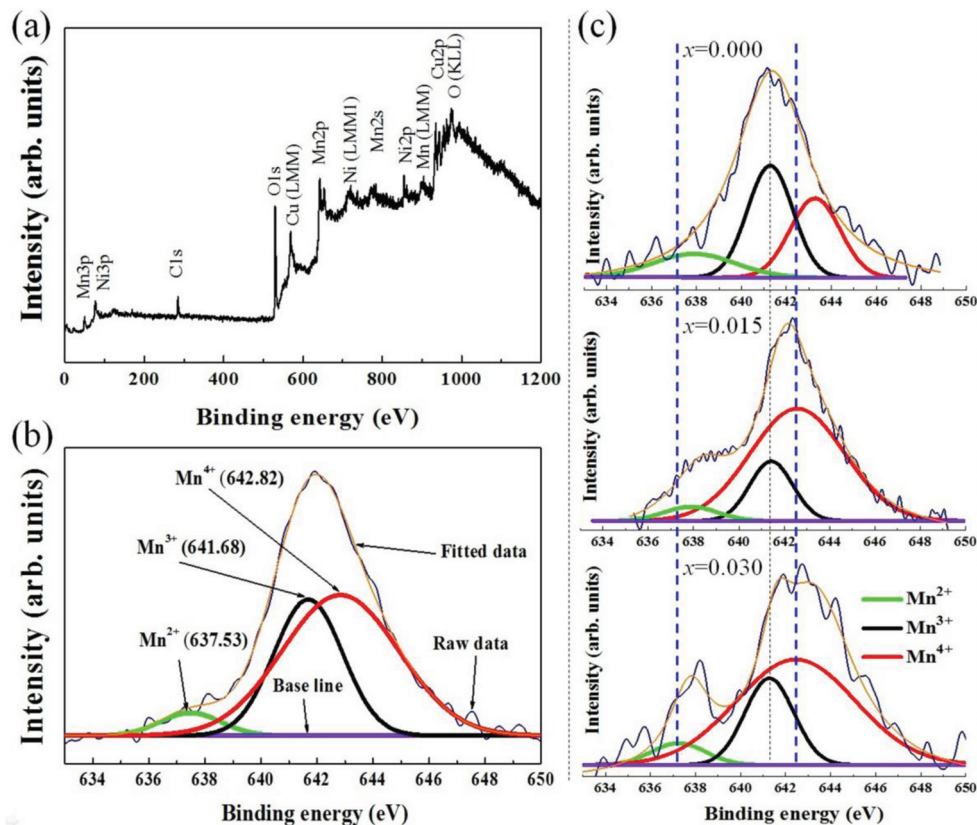


Figure 8. (a) XPS spectra and (b) $\text{Mn}2p_{3/2}$ core level of the sample with $x = 0.010$. This $\text{Mn}2p_{3/2}$ region was divided into three peaks, corresponding to Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively. (c) the Mn^{2+} and Mn^{4+} peaks of the Cu-containing films ($x = 0.015$ and 0.030) shifted toward lower BE values, compared to those of the Cu-free one ($x = 0.000$).

Table 3. Characteristics of the XPS $\text{Mn}2p_{3/2}$ spectra of films.

x	Binding energy (eV)			Peak intensity (area %)			
	Mn^{2+}	Mn^{3+}	Mn^{4+}	Mn^{2+}	Mn^{3+}	Mn^{4+}	$\text{Mn}^{3+}/\text{Mn}^{4+}$
0.000	637.94	641.69	643.29	21.70	34.18	44.12	0.77
0.015	637.80	641.71	642.72	12.68	25.87	61.45	0.42
0.020	637.51	640.76	642.71	8.89	28.65	62.46	0.45
0.030	637.45	641.68	642.70	2.00	26.24	71.76	0.36
0.035	636.78	641.37	642.54	4.51	19.70	75.79	0.24

created by the Ni ions alone in the Cu-free. In copper-containing nickel-manganite spinels, monovalent copper (Cu^{1+}) has been assigned to reside in the tetrahedral site while bivalent copper (Cu^{2+}) occupies both the octahedral and tetrahedral sites of the spinel [41–43]. The presence of Cu^{1+} leads to an increasing amount of cations in the tetrahedral sub-lattices, which induces the displacement of some Ni^{2+} cations from tetrahedral to octahedral sites. This process causes the production of Mn^{4+} on octahedral sites to maintain the electrical neutrality. The Mn^{4+} ion that is thereby created, and consequently explains its concentration observed in Table 3. As more Mn^{4+} ions are generated, a large number of localized electrons are produced, and hence this could be addressed as the main reason for the improved carrier concentration which contributes to the electrical conductivity of the studied films.

We observed that the mobility of the charge carriers decreased in the rich Cu-compositions in spite of their increased grain size (see Table 1), possibly due to the ionized Cu atoms acting as scattering centers at high N , and thereby reducing μ . Eventually, the conduction was associated with changes in N , caused by the defects and structure, rather than by grain size. For the case of $x \geq 0.035$, because of the pore surface of the films as shown in Figure 2(g, h), μ rapidly dropped, which was ascribed to the increase in ρ_{300} , even though a large N (see Table 3) has been detected in those films.

Huang et al. reported that the optimal electrical conductivity of spinel films with a composition of $\text{Mn}_{1.4}\text{Co}_{1.0}\text{Ni}_{0.6}\text{O}_4$ [15] was attained only was nearly unity. In the present study, this ratio was, however, found to be lower than unity, and tended to further decreased with increasing Cu level (see Table 3), similar to the case of $\text{Ni}_{0.79}\text{Mn}_{2.21}\text{O}_4$ bulk ceramics which was examined as a function of sintering temperature [44]. In our experimental system [19,20], the samples with highly conductive properties commonly possessed the ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ lower than unity. This is most likely due to the fact that the film compositions were not optimized. The ICP-OES data of the present specimens showed the co-presence of the three metallic elements: Mn, Ni, and Cu in films

(Table 1), where the Cu content in the solid films proportionally increased with that in the solution (x). However, the total mass portion of both Ni and Cu was relatively lower whereas that of Mn was much higher, compared to the case of the common spinel nickel-manganite-based solid compounds [4,11,15,17,26,31,34,38,44]. During our previous practical investigation, we found that the introduction of transition elements such as Ni, Co and/or Cu into the Mn matrix through LFD, was effective for enhancing the conductive behavior of the resulting Mn_3O_4 -based films which has demonstrated a continuously improved trend. Unfortunately, the conductivity was limited by the poor microstructures since the compositions contained high degrees of substitution elements. This led to challenges in controlling compositions of the films when using LFD, while imposing the requirement of keeping dense, smooth and homogenous film bodies. Nevertheless, we believe that this approach offers some promise for producing Mn_3O_4 -based films with high electrical performances.

3.4. Electrical stability

In this work, we also examined the change in RT resistance with time to demonstrate the electrical stability of the films. It has been reported that the aging coefficient ($\Delta R/R$) of nickel-manganite films was in the range of 2 ~ 20% over a period of ~500 h at 150°C in air [45]. Our aging result (Figure 9) showed that the $\Delta R/R$ was 6.8% for the Cu-free film. As x increased, the $\Delta R/R$ continuously increased up to 11.3% while that for the best conductive specimen ($x = 0.025$) was 10.5%. These aging behaviors were worse compared to those of the undoped nickel-manganite films prepared by spin-spraying, annealed at 400°C in Ar [46]. Previous investigations [47,48] demonstrated Cu as one of the most effective ion for lowering the resistivity but Cu doping otherwise degraded the electrical stability of the nickel-manganites.

Chen et al. also reported that the Cu doping caused a decrease in the resistivity of $\text{Ni}_{0.5}\text{Mn}_{2.5}\text{O}_4$ ceramics to 70 Ω cm, but simultaneously raised the resistivity drift up to 14.9% [49]. Fortunately, Zn was demonstrated to effectively stabilize the spinel structure against the oxidation reaction when partially replacing Mn in nickel-manganite compounds [50,51]. Thus, the fact that Zn addition reduces the resistance drift ($\Delta R/R$), can prompt the investigation of compositional modification with Zn to be carried out, which will be addressed in our next studies.

4. Conclusion

The NTCR manganite Mn_3O_4 -based thin films have been prepared from aqueous solution $(\text{Ni}_{0.2}\text{Mn}_{2.8-x}\text{Cu}_x)\text{Cl}_2$ ($x = 0.010 \sim 0.040$) via a liquid flow deposition (LFD) route. The heat treatment at 400°C in air enabled a transformation from amorphous to a cubic spinel structure, which significantly contributed to the electrical conduction of the films via the small-polaron hopping mechanism. Crystallinity, grain size and carrier concentration increased with the increase in copper content. Notably, the addition of Cu at a dosage as low as 2.5 mol% effectively decreased the electrical resistivity (ρ) of films down to 200 $\Omega\cdot\text{cm}$, while the absolute temperature coefficient of resistance at room temperature (TCR_{300}) was retained larger than 2.38%K⁻¹. This electrical performance combined with the modest temperature synthesis highly confirmed a promising of the resultant thin films for use in microbolometers.

Highlights

- The single cubic spinel phase was found in all the films annealed at 400 °C.
- The films possessed an NTCR characteristic with $\text{TCR} = 2.38 \sim 3.21\%\text{K}^{-1}$.
- The replacement of manganese by copper (Cu) caused a significant improvement of electrical properties of the annealed films.

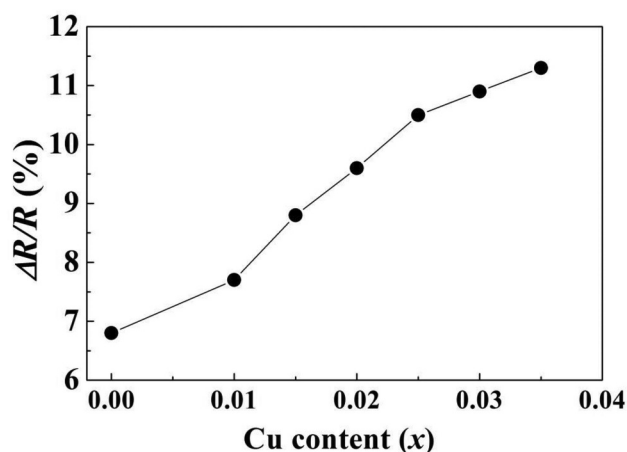


Figure 9. Sheet resistance drift versus Cu level of the films after 500 h of aging at 150°C in air.

- The best film exhibited a modest electrical resistivity (ρ) of 200 $\Omega\cdot\text{cm}$.

Disclosure statement

No potential conflict of interest was reported by the authors.

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