

Annealing temperature dependent structural and electrical properties of (Mn,Ni,Co)₃O₄ thin films

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ABSTRACT

Here, we demonstrated that polycrystalline (Mn,Ni,Co)₃O₄ films with a high negative temperature coefficient of resistance (NTCR) behavior can be achieved at low annealing temperatures (≤ 400 °C) via a liquid flow deposition method. The processing conditions applied to obtain the high-quality films were investigated with focus on the flow rate of the oxidizing agent (H₂O₂) and annealing temperature (T_a). The introduction of an appropriate amount of H₂O₂ solution into the deposition system led to the partial oxidation of Me²⁺ ions (Me = Mn, Ni and Co) to Me³⁺ which subsequently adsorbed to the films, with only little effect on the film surface quality. The pre-existing Mn³⁺ ions enabled the possibility of reducing the final annealing temperature to 300 °C for the film crystallization with a pure cubic spinel phase. We also studied the dependence of the electrical properties on the T_a in the range of 285–400 °C. It was found that the films were highly conductive and showed a typical NTCR characteristic at annealing temperatures of 300 °C and above. Notably, at $T_a \geq 350$ °C, the films exhibited an absolute temperature coefficient of resistance (TCR) exceeding 2.43% K⁻¹ together with a moderate resistivity (ρ) of < 3 k Ω cm, indicating their excellent potential for application in infrared detectors. In addition, the films showed good electrical stability with time, as their aging coefficient ($\Delta R/R_0$) varied in a range of 5.9–6.4% after 500 h of aging in air at 150 °C. To the best of our knowledge, there have been no reports on cubic spinel Mn₃O₄-based thin films at temperatures below 400 °C.

1. Introduction

Spinel oxides with the general AB₂O₄ formula are a group of transition metal oxides which have interesting electronic and magnetic properties and thus are suitable for various technological applications [1–6]. Among them, manganite (Mn₃O₄)-based oxides that exhibit the negative temperature coefficient of resistance (NTCR) characteristic have been of technological interest owing to their unusual electrical properties that permit the uses in temperature sensors and infrared (IR) detectors [7]. The basic Mn₃O₄ oxide (hausmannite) is known to possess a tetragonal spinel structure with Mn²⁺ and Mn³⁺ ions occupying the A (tetrahedral) and B (octahedral) sites, respectively, and it commonly shows intrinsic insulating properties [8]. However, the incorporation of appropriate transition metal ions into the spinel Mn₃O₄ matrix causes a change in the crystal structure, leading to a remarkable improvement in its electrical properties. In particular, cubic closed packed oxygen spinel structure has been found in the Mn₃O₄-based modified with nickel, cobalt and/or copper, allowing both the

resistivity and temperature coefficient of resistance (TCR) to be tailored [9]. It has been found that the partial replacement of Mn ions by other transition metal ions (e.g., Ni, Co and Cu) at both tetrahedral and octahedral sites alters the spinel structure from its normal state to mixed state, enhancing the possibility for Mn to adopt multiple oxidation states [10,11]. The conduction mechanism of such a material is normally explained in terms of the electron hopping between Mn³⁺ and Mn⁴⁺ states at the octahedral sites [12,13]. Apart from the redistribution of cations, the valence state of the constituent metal ions (Mn and other dopants) in the as-prepared materials is of great importance, as it plays a crucial role in the formation of the crystal structure, and thus, in the tailoring of the electrical properties. In reality, this factor strongly depends on the processing aspects, i.e., raw materials, composition, synthetic conditions and annealing temperature, which are completely determined by the preparation method [14–16].

Nowadays, there has been renewed interest in the thin film forms of Mn₃O₄-based oxides due to their advantages of stability, reproducibility, and fast output responses, as compared to the bulk and thick film

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counterparts [17,18]. There are various techniques for the preparation of thin films [19–24], of which the low processing temperature approaches have attracted immense attention because of their cost-effectiveness, simplicity, and capability to facilitate large area coverage. Nevertheless, a film prepared at a low temperature usually requires a post annealing process as a second step for the crystallization of the material, so as to improve its electrical conductivity and stability. Obviously, an easy integration of thin films into an ultimate device such as microbolometer requires the annealing temperature to be as low as possible to avoid any practical difficulties. Therefore, the exploration of low processing temperature methodologies that enable the preparation of crystallized Mn_3O_4 -based thin films has been worth attempting.

Regarding the spinel phase of the Mn_3O_4 -based compositions, Wickham et al. built a phase diagram at temperatures above 600 °C for the nickel manganite ceramic bulk system [25]. The authors reported that a cubic spinel phase could form in materials with suitable compositions at a minimum sintering temperature of 705 °C. Later, Tang and co-workers constructed an expanded phase diagram at lower temperatures to investigate the possible cubic spinel region of oxalate-derived manganite powders [26]. It was revealed that the metastable spinel phase could form below 400 °C but was then oxidized and decomposed into NiMnO_3 and Mn_2O_3 , at the elevated temperature of 400–750 °C. In practice, typical spinel ceramics were produced through a sintering process at typical temperatures of 850–1250 °C [27], while most existing works demonstrated the crystallization at the temperatures above 500 °C for the thin films [28]. Several attempts have been made to lower the critical temperature for crystallization of thin films, however the electrical performance of the obtained final products have been poor [29].

It is known that the $\text{Mn}^{3+}/\text{Mn}^{2+}$ ratio is one of the critical factors for the crystallization of spinel manganite films derived from hausmannite Mn_3O_4 with the general formula AB_2O_4 , consisting of Mn^{2+} and Mn^{3+} cations [30]. Since most synthesis techniques at low temperatures (solution-based routes) such as chemical solution deposition [19], chemical bath deposition [20], ferrite plating [21], dip coating [22], and etc, utilize the solutions with Mn^{2+} cations as the starting precursor, the as-grown films consist only of Mn^{2+} ions after deposition. Consequently, it is crucial to oxidize Mn^{2+} to Mn^{3+} for the formation of spinel phase which must be performed in the solid state through a series of reactions between Mn^{2+} and oxygen during annealing process. The heat energy provided during annealing must suffice for facilitating (i) the oxidation of Mn^{2+} to Mn^{3+} and (ii) re-arrangement of cations in the lattices in order to form a crystal. It is considered that, if the Mn^{3+} ions are available in the as-prepared state of the films, the thermal energy required for crystallization would be lower, because no more (or less) $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ oxidation reactions are required and thus the annealing temperature can be reduced. To confirm this hypothesis, Mn_3O_4 -based thin films have been prepared by the liquid flow deposition (LFD) route developed by us and reported elsewhere [31]. The results showed that Co–Ni–Mn–O oxides with the cubic spinel-type structure are formed at 400 °C, yielding highly conductive films [32]. The facile formation of Mn^{3+} (and also Ni^{3+} and Co^{3+}) ions via chemical reactions of Mn^{2+} (also Ni^{2+} and Co^{2+}) with an oxidizing agent (H_2O_2) in the liquid solution was highlighted as the key aspect of the successful fabrication of those polycrystalline films. The advantage comes from the fact that the oxidation of Mn^{2+} to Mn^{3+} is much easier to accomplish in the liquid state, rather than in the solid state as in common cases. Actually, the film structure and morphology are strongly dependent on the amount of trivalent manganese ions present in the solution, which is directly affected by the supplied oxidizing source. This is the reason why the LFD technique was chosen, in which the flow rate, concentration, and pH of both the reactant and oxidizing solutions, as well as the substrate temperature can be reasonably controlled, so that $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ oxidation occurs without precipitation (which is detrimental to the film surface quality) in the deposition chamber. Those factors eventually allows the formation of smooth films

with co-existing Mn^{2+} and Mn^{3+} ions via a heterogeneous nucleation mechanism. In addition, LFD is known to be a solution-based process with many advantages, such as not requiring vacuum, low-energy consumption, and environmental friendliness, that ensures cost effectiveness and allows the use of various substrate types [33].

The fact that the preparation of thin films at low processing temperatures and the specific properties of such films have been rarely reported so far, led us to investigate the possibility of preparing the spinel Mn_3O_4 -based films at temperatures below 400 °C. Accordingly, thin films of spinel Mn_3O_4 doped with Ni and Co were deposited from a $(\text{Mn}_{2.77}\text{Ni}_{0.20}\text{Co}_{0.03})\text{Cl}_2$ solution via LFD with an optimal concentration of the oxidizing agent. The morphology, structure, and electrical properties of the best films were investigated with emphasis on the influence of the annealing temperature. In addition, the aging behavior was examined to investigate the stability feature of the prepared films.

2. Experimental procedure

A solution with the composition of $(\text{Mn}_{2.77}\text{Ni}_{0.20}\text{Co}_{0.03})\text{Cl}_2$ used for the preparation of thin films was prepared as follows: 29.239 g of MnCl_2 , 2.535 g of NiCl_2 , and 0.380 g of CoCl_2 (Sigma–Aldrich) were dissolved in 3200 mL deionized water with stirring at room temperature (RT). After the preparation of this solution, 17.117 g of NH_4Cl (Kanto Chemical) was added and mixed for 2 h. The thus-obtained homogeneous aqueous solution was used as the precursor solution for thin film deposition. The pH of the solution was adjusted with ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$) to 6.75–6.90 during deposition.

The films were deposited on commercial Si wafer ($2.5 \times 2.5 \text{ cm}^2$) substrates via the LFD technique as illustrated in Fig. 1. This method was described in great detail in our previous publication [31]. The piranha cleaning method was applied to remove all organic matter and to hydroxylate the Si substrate surfaces, making them extremely hydrophilic [34]. The reaction solution was flown into the deposition chamber at a speed of 400 mL/h, simultaneously with an oxidizing solution. In this work, we varied the flowing speed (α) of the oxidizing solution as 25, 50, 75, 100, 125, and 150 (mL/h). During the deposition, the precursor solution was continuously stirred and the substrate temperature was maintained at 60 °C. The deposition duration was set as 8 h for all samples. After their deposition, the films were washed with deionized water, and then dried at 100 °C for 2 h in an oven. Finally, the selected specimens were annealed at 285, 300, 350, 375, and 400 °C for 5 h in air (at 5 °C/min heating rate).

An X-ray diffractometer (XRD; Rigaku, Japan) was used to determine the crystal structure of the films. An atomic force microscope (AFM; Neos, Bruker, Germany) and a field-emission scanning electron microscope (FE-SEM; JEOL, Japan) were used to examine the surface morphology of films. The oxidation states of manganese were characterized with an X-ray photoelectron spectrometer (XPS; VG ESCA 3000, Microtech, UK). A Hall effect measurement system (HMS-3000) was used to investigate the carrier concentration and mobility. The sheet resistance of the films was measured using a four-point probe system (VP75, DSF system, Doosung, Korea) composed of a probe station, a custom-built automated data acquisition system, and a computer-controlled source meter. A heated stage was also applied to obtain data at different temperatures over the range of 22–115 °C. For the stability test, the films were aged in an oven at 150 °C (in air) and the room-temperature sheet resistance was measured at various points during aging, up to a duration of 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.

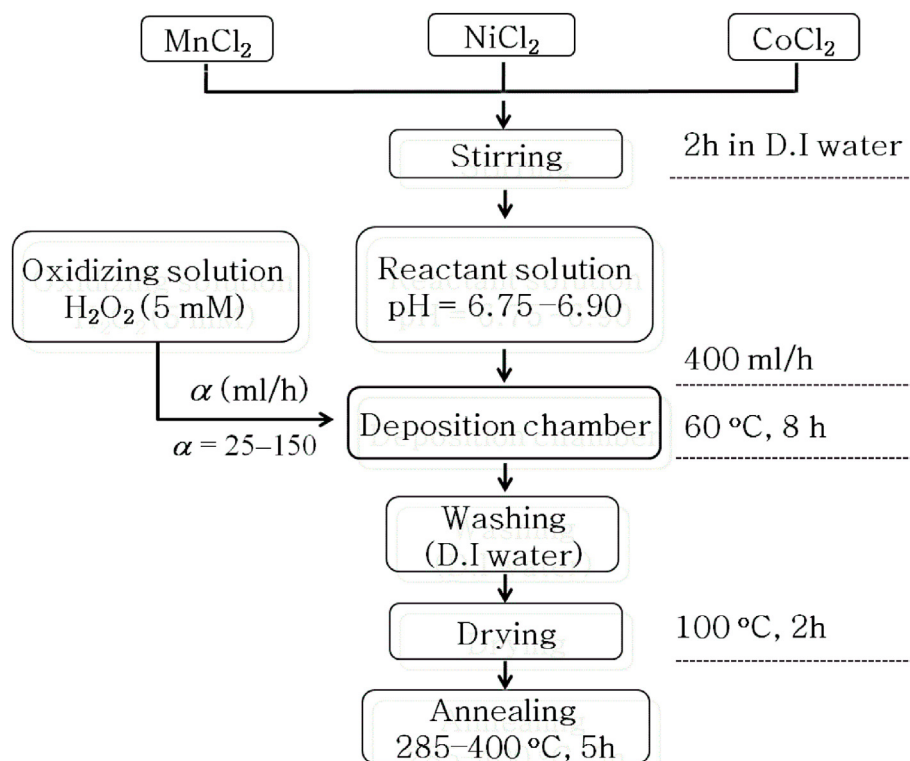


Fig. 1. Flow diagram for thin films prepared from chloride solution using the liquid flow deposition method.

3. Results and discussion

3.1. Optimization of the flow rate of the oxidizing agent for thin film synthesis

It has been found that the microstructure of as-grown films deposited using a MnCl_2 -based precursor depends on many factors such as the type of oxidizing agent and its quantity, composition and concentration of the reaction solution, solution pH, and deposition temperature. Here, Ni and Co (at small fractions) were selected to tailor the electrical properties of spinel Mn_3O_4 , and we focused on studying the roles of the oxidizing agent and its amount on the film formation. Theoretically, the activation energy barrier for heterogeneous nucleation (ΔG_{het}) is generally lower than that for homogeneous nucleation (ΔG_{hom}) [35]. As the deposition of the film onto a substrate surface involves heterogeneous nucleation, if the change in the Gibbs free energy of the solution for liquid $\rightarrow$ solid phase transformation is $\Delta G = G_{\text{Liquid}} - G_{\text{Solid}}$, the ΔG of film formation should follow the order of $(\Delta G_{\text{het}}) < (\Delta G) < (\Delta G_{\text{hom}})$. In practice, upon the introduction of an oxidizing reagent into the system, the color of the solution changes from dark pink to brown red, which is believed to be mainly caused by the formation of Mn^{3+} cations. The $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ oxidation reaction has been performed not only in film but also in solution, leading to changes in the Gibbs free energy of the system, which consequently enables homogeneous nucleation of the oxide in solution. The bulk precipitates formed in solution as the products of the growth of the formed homogeneous nuclei cause a change in the color of the solution. Consequently, for the deposition of films (heterogeneous nucleation), the oxidation of Mn^{2+} into Mn^{3+} cations is necessary, but precipitation should be prevented. During the course of our investigation, we found that the time at which precipitation occurs varies depending on the amount of the oxidizing reagent used, and thus, it is acceptable if the precipitates form after leaving the deposition chamber (Fig. 1). In such a case, the introduction of a reasonable amount of the oxidizing reagent, which corresponds to the minimum amount required to start the solution color change (in the deposition chamber) will allow the growth

of films without contamination. Therefore, we qualitatively optimized the amount of oxidizing reagent during the film deposition by performing a series of experiments using $(\text{Mn}_{2.77}\text{Ni}_{0.20}\text{Co}_{0.030})\text{Cl}_2$ solution. In these experiments, the solution color in the deposition chamber was individually observed through a transparent glass cover, while the flow rate of the oxidizing solution was changed in steps from 25 to 50, 75, 100, 125, and 150 (mL/h) under constant temperature, solution pH, solution concentration, solution flow rate, and oxidant concentration, as shown in Table 1. The following two points should be noted: (i) although sodium nitrite (NaNO_2) has been reported as the most suitable oxidizing reagent for the deposition of ferrite films [36], the solution color did not change with this oxidant in the present study; however, the solution color changed with the use of hydrogen peroxide (H_2O_2). This confirms the results of a previous article [37], in which the order of the standard oxidation potential of the materials is NaNO_2 (0.9 V) $<$ $\text{Mn}^{2+}/\text{Mn}^{3+}$ (1.51 V) $<$ H_2O_2 (1.8 V), and thus only H_2O_2 can oxidize Mn^{2+} to Mn^{3+} . Next, (ii) with the use of H_2O_2 (5 mM) as the oxidizing agent, there is no change in the solution color when its flow rate, α is ≤ 100 mL/h. In contrast, the change in the solution color to brown-red was observed at $\alpha > 100$ mL/h. The thin films obtained with these various α values were also compared in terms of their microstructure observed by the FE-SEM (Fig. 2). It is seen that there are no significant differences in the morphology among films deposited with $\alpha = 25, 50, 75$, and 100 mL/h. Nevertheless, the film surface seems to become slightly rougher with increasing H_2O_2 solution flow rate, with some foreign bulk materials being found in films formed at

Table 1
Thin film synthesis conditions.

Substrate temperature (°C)	60
Solution composition	$(\text{Mn}_{2.77}\text{Ni}_{0.20}\text{Co}_{0.030})\text{Cl}_2$
Solution pH	6.65–6.85
Reactant solution rate (mL/h)	400
Oxidizing solution concentration (mM)	5 mM

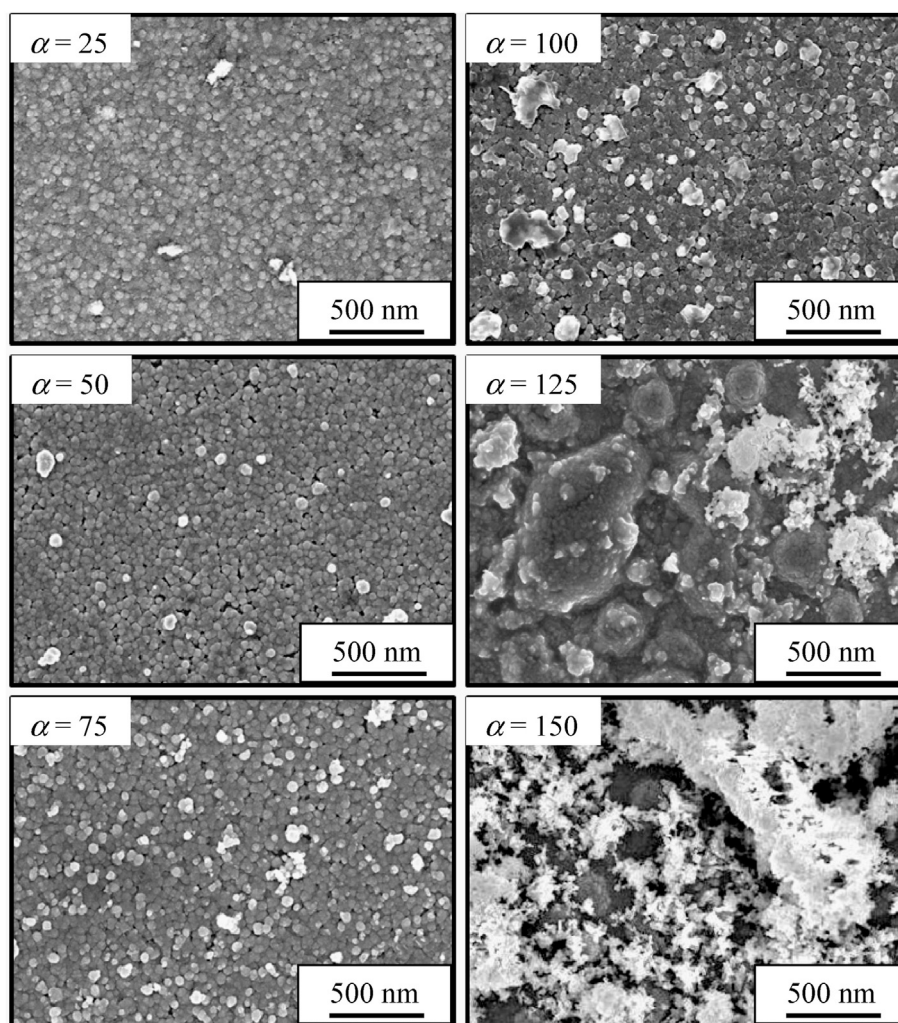


Fig. 2. Top view FE-SEM micrographs of thin films prepared at different oxidizing solution flow rate (α).

higher α . At higher H_2O_2 solution rates, the formation of discrete agglomerates rather than a uniform film was observed ($\alpha = 125$ mL/h), and the substrate surface was mostly covered by a large amount of precipitate ($\alpha = 150$ mL/h). The particle agglomeration and precipitation degrade the film quality, which confirms our hypothesis that the films should be deposited just before the solution color changes in the deposition chamber. As the smooth microstructure of films is known to be a primary requirement to ensure the reliability of practical devices, the film deposited with $\alpha = 100$ (mL/h) was selected for further investigation in this work.

3.2. Analysis of the microstructure

The microstructural characteristics of the as-prepared and annealed films were analyzed by the AFM and FE-SEM, as shown in Fig. 3. It is seen that the as-prepared film shows a sub-nanograin structure with 40–80 nm grains (Fig. 3a) and has a thickness of approximately 450 nm (Fig. 3i). Larger grains are revealed in Fig. 3b–d, which were formed after thermal treatment at different temperatures. Fig. 3j shows an AFM three-dimensional (3D) topographical image of a film annealed at 375 °C. The image indicates a grain size of approximately 130–300 nm, which further confirms and supports the grain growth through annealing, as presented in Fig. 3b–d. Fig. 3e–h shows the corresponding grain size histograms for estimating the average grain size in the films in Fig. 3a–d. The average grain sizes are 52.4, 107.8, 166.5, and 216.4 nm for the as-prepared film and the films annealed at 285, 350,

and 400 °C, respectively. These results indicate that the average grain size increases with increasing T_a , which is attributed to the higher thermal energy at higher T_a , which enables the diffusion of ions, leading to grain enlargement and microstructure coarsening [38]. Further, the average roughness (R_a) of film surfaces was calculated and the results are summarized in Table 2. It is found that R_a tends to increase from 32.6 for as-prepared sample to 86.3 nm for sample annealed at 400 °C, confirming the fact that grain enlargement leads to a rougher surface of the thin films.

3.3. Structural analysis

Fig. 4a shows the XRD patterns of as-deposited and annealed thin films. Only broad humps are observed in the XRD pattern of the as-deposited specimen, indicating their amorphous nature, despite the presence of both Me^{2+} and Me^{3+} cations ($\text{Me} = \text{Mn}, \text{Ni}, \text{and Co}$), as confirmed by the XPS data in Fig. 5. For the film annealed at 285 °C, the XRD humps are reduced, possibly due to the complete evaporation of the chloride compounds, but no distinct peaks are observed. In contrast, peaks appear in films fired at 300 °C and above, indicating the polycrystalline nature of the films on the Si substrates. The XRD result is in accordance with the standard card data of cubic spinel NiMn_2O_4 (JCPDS card No. 84-0542). No other secondary phase could be detected, which implies that only a single phase of cubic spinel structure was formed from the amorphous film through heat treatment. Apart from the (311) peak with the highest intensity due to the preferential

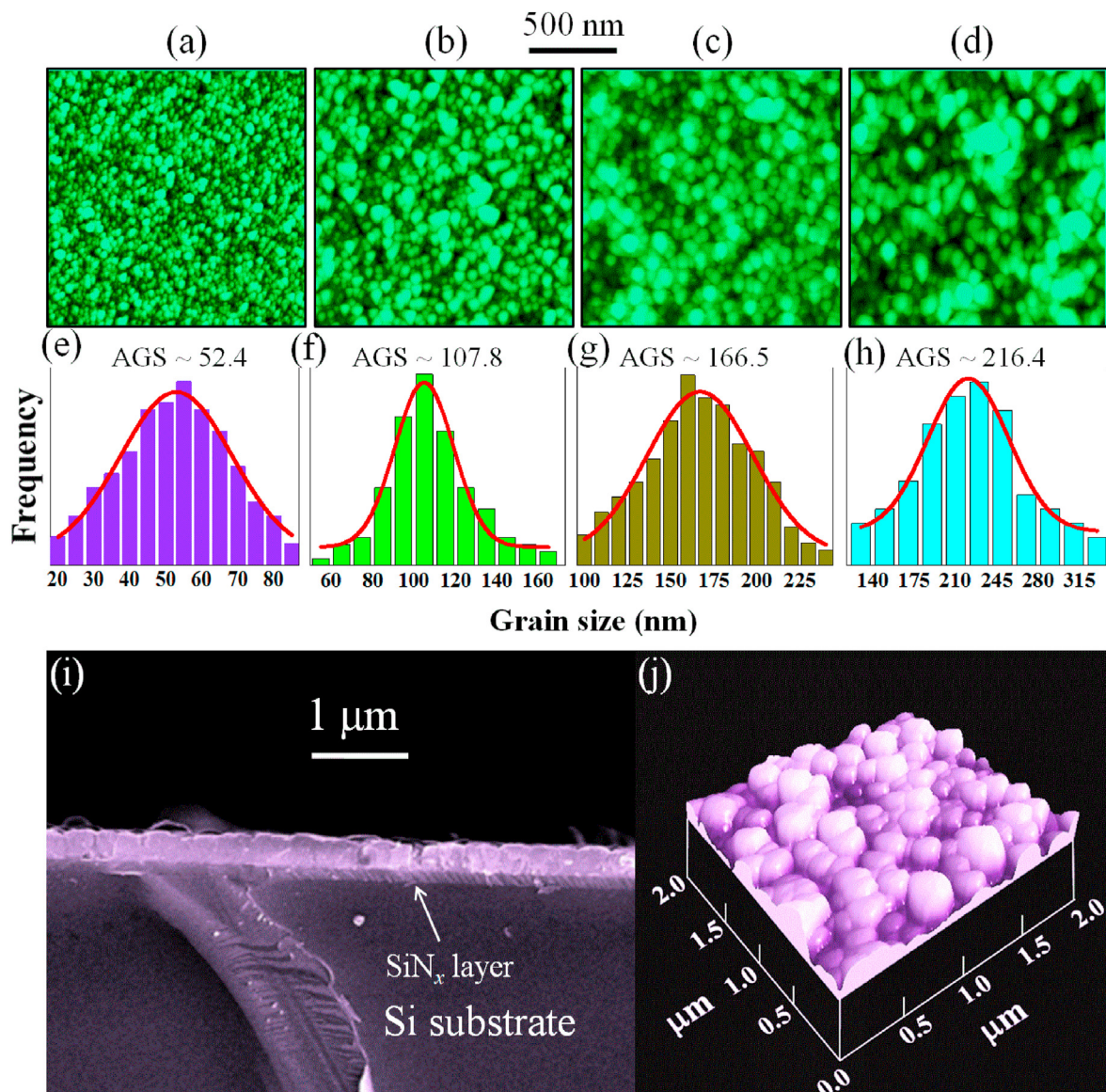


Fig. 3. AFM image of the films (a) as-deposited, (b–d) annealed at different temperatures: 285 °C, 350 °C and 400 °C. (e–h) The grain size histograms showing its distribution and average grain size of the corresponding samples in Figs. (a–d). (i) FE-SEM cross sectional image of as-deposited sample and (j) three-dimensional (3D) AFM topographical image of film annealed at 375 °C.

Table 2

Thin film properties, examined as a function of annealing temperature (T_a).

Sample No	Annealing temperature, °C	Crystallite size, nm	Roughness (R_a , nm)
1	As-prepared		32.6
2	285		
3	300	6.18	59.5
4	350	9.04	67.8
5	400	14.43	86.3

The average grain size was evaluated from the histogram measured by AFM. The roughness was calculated using an AFM scanning probe image processor (SPIP-4.8.2) software included in the AFM instrument.

The average crystallite size (D) was evaluated by using Scherrer's formula [40]:

$$D = \frac{(0.9\lambda)}{(\beta \cos \theta)}$$

where λ is the wavelength of X-ray (1.5406 Å), β is the full width at half maximum in radians and θ is the angle of diffraction.

film orientation along the (311) crystal plane, other peaks corresponding to (111), (220), (222), (400), (422), (511), and (440) planes are also observed, but with low relative intensities. The temperature of 300 °C that enables the observation of spinel peaks in the XRD pattern of films deposited in this work is far below the typical sintering temperature (850–1250 °C) of conventional ceramics [27] and the annealing temperature (500–750 °C) of the common thin films [17,28,29,38]. In our case, the samples annealed at 450 and 500 °C also exhibit the same XRD characteristics (not shown here) as those of samples annealed at 300–400 °C, shown in Fig. 4a, except that the XRD peak intensities are higher. This result implies that decomposition by oxygen did not occur when the films were heated at 400–500 °C, and thus, the obtained films are believed to have a stoichiometric spinel phase. With the elevation of T_a , the intensity of the (311) peak increases, implying improved crystallinity of the film, probably because the high thermal energy provided by high annealing temperature induces the crystallites to orient in appropriate equilibrium sites, consequently promoting the crystallinity and orientation levels of the film [39]. In addition, the full width at half maximum (FWHM) of the (311)

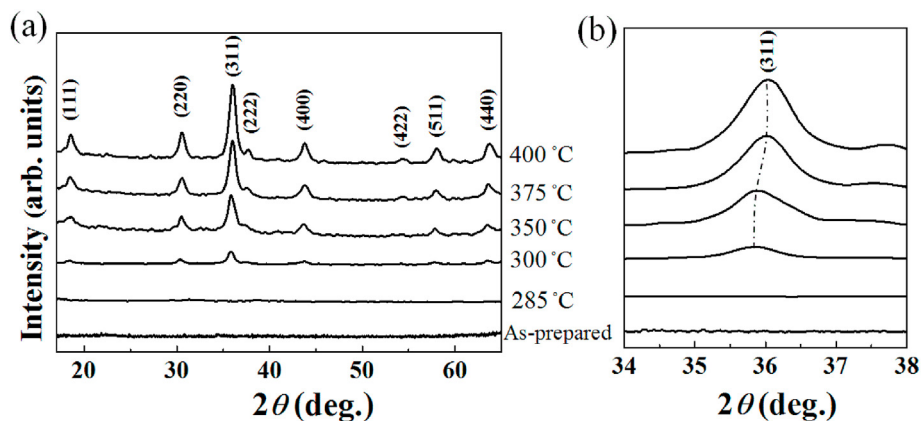


Fig. 4. a) X-ray diffraction analysis of the films, examined as a function of annealing temperature (T_a) and b) shift in the (311) peak with T_a .

peak tends to decrease with increasing annealing temperature, which is attributed to the coalescence of crystallites at higher temperatures. This is also confirmed by the observation that the average crystallite size (D), calculated using Scherrer's formula [40], increases from 6.18 to 14.43 nm when the annealing temperature is increased from 300 to 400 °C, as shown in Table 1. On the other hand, the (311) peak shifts towards higher angles with increasing T_a , as indicated by the black dashed line in Fig. 4b, indicating a decrease in the lattice parameter [41]. As the atomic radius of manganese (1.37 Å) is larger than those of nickel (1.35 Å) and cobalt (1.25 Å) [42], it is reasonable to understand that the lattice parameter decreases due to the diffusion of more nickel and cobalt ions into the lattice of Mn_3O_4 at high firing temperatures. Otherwise, since the samples were annealed in air, the decrease in

lattice parameter of the spinel may relate to the formation of oxygen deficiencies [43–45] and/or the oxygen vacancies [46,47].

3.4. XPS analysis

The oxidation states of the elements in the studied samples were analyzed by the XPS. Fig. 5a shows the XPS survey scan of the as-prepared film; all the peaks can be assigned to Mn, Ni, Co, O, and C. In our case, the peak of C originates from foreign hydrocarbons of the XPS instrument itself. In order to identify the oxidation states of Mn, Ni, and Co, the high-resolution XPS $2p_{3/2}$ profiles were examined and fitted as displayed in Fig. 5b–d. The results indicate two peaks for each metal element, which could be assigned to three oxidation state pairs: Mn^{2+}

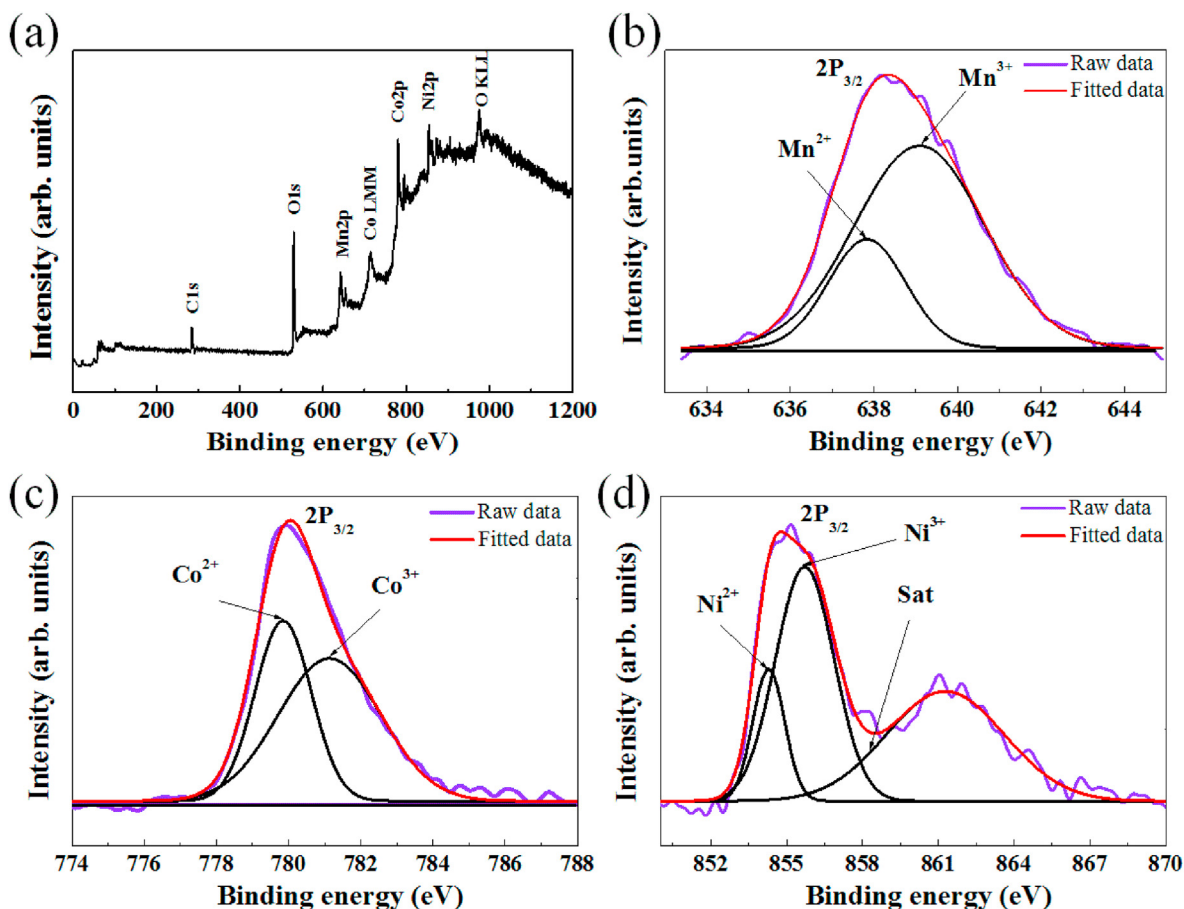


Fig. 5. XPS characterization of as-prepared $(Co,Ni,Mn)_3O_4$ film: (a) XPS survey spectrum and high resolution XPS spectra of (b) $Mn 2p_{3/2}$, (c) $Co 2p_{3/2}$ and (d) $Ni 2p_{3/2}$.

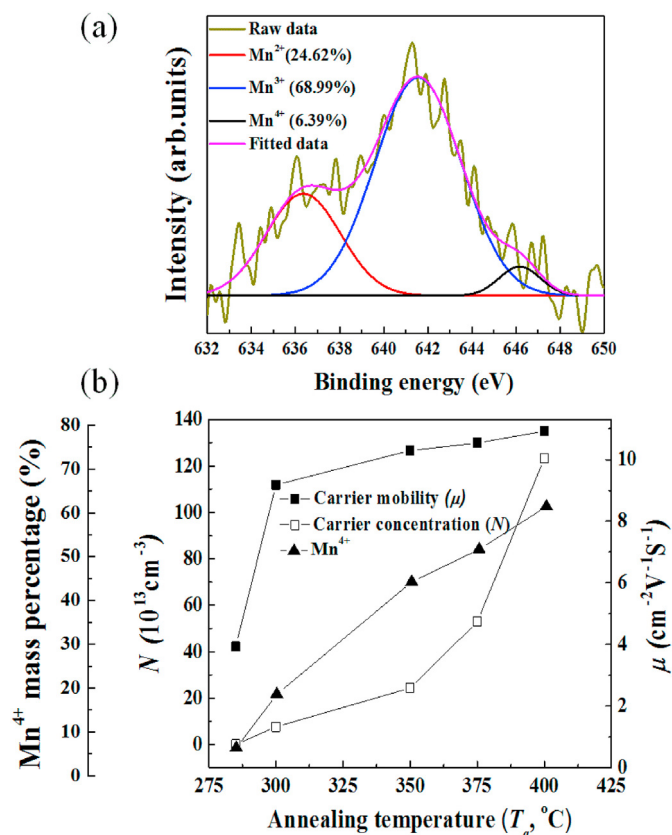


Fig. 6. (a) Mn 2p_{3/2} XPS profile of the film annealed at 285 °C. (b) Variation of Mn⁴⁺ concentration, carrier concentration, and Hall mobility in film as a function of annealing temperature (T_a).

and Mn³⁺ [48] (Fig. 5b), Co²⁺ and Co³⁺ [49] (Fig. 5c), and Ni²⁺ and Ni³⁺ [50] (Fig. 5d). Therefore, it is reasonable to conclude that all the metal elements, Mn, Ni, and Co have 2+ and 3+ valence states in the as-prepared sample. The presence of mixed cations suggests that Mn²⁺, Ni²⁺, and Co²⁺ were partially oxidized to Mn³⁺, Ni³⁺, and Co³⁺, respectively, during the deposition of films. In addition, although manganese has various oxidation states (2+ to 7+), the results obtained here (Fig. 5b) clearly confirm that the oxidation of Mn²⁺ with H₂O₂ results in only Mn³⁺ under the present experimental conditions. We believe that these pre-existing Mn³⁺ ions induce the formation of the spinel structure under the provision of heat energy, as demonstrated by the XRD data of the annealed samples in Fig. 4. On the other hand, Mn⁴⁺ cations are detected in the samples annealed at 285 °C, as shown

in Fig. 6a, which illustrates that Mn³⁺ is further oxidized to Mn⁴⁺ at a temperature as low as 285 °C. Furthermore, the Mn⁴⁺ concentration increases with increasing T_a as presented in Fig. 6b, that is in good agreement with the XRD results. The increase in the Mn⁴⁺ concentration can be attributed to two possible reasons: (i) when T_a increases, nickel and cobalt are more likely to diffuse into the lattices of the spinel which enables the migration of the Ni²⁺ cations from the octahedral sites to the tetrahedral sites, and thus the Mn⁴⁺ cations are generated for charge compensation [12,17,19,26,27,38]. (ii) the increase in T_a provides the higher thermal energy which leads some Mn³⁺ to be oxidized to Mn⁴⁺ cations via the reactions with oxygen. Fig. 6b also depicts the carrier concentration (N) and carrier mobility (μ), determined by using a Hall-effect measurement system. The measured data shows negative charge values for the film series, demonstrating an unambiguous the n-type nature and the electrons are therefore assigned to the major carriers. This is consistent with the result reported by Jiang. et al. [51], even though the Mn–Co–Ni–O ceramic system has been considered as a p-type semiconductor [52]. As shown in Fig. 6b, the elevation of T_a from 300 to 400 °C results in an increase of N from 7.57 × 10¹³ to 123.35 × 10¹³ cm⁻³. The improvement of N is most likely attributed to the increase in the Mn⁴⁺ portion (from 6.39 to 61.43%). This is because more Mn⁴⁺ cations produce a larger number of sites for electron hopping between Mn³⁺ and Mn⁴⁺ [9,26,27]. We also suggest that the electrons may additionally transport (hopping) via the Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ pairs along with the Mn³⁺/Mn⁴⁺ pairs in the octahedral sites. On the other hand, μ increases from 3.9 to 9.18 cm²/V·s when T_a rises from 285 to 300 °C. The rapid change in μ demonstrates a significant difference in carrier transport ability between non-crystallized and crystallized states. Meanwhile, it has been reported that the larger grain size commonly induces the carrier mobility, due to the grain boundary effect [53–55]. However, only little changes in μ can be observed in the range of T_a = 300–400 °C, regardless of their enlarged grains as shown in Fig. 3. Therefore, it should be noted that the carrier mobility is mainly determined by the crystal structure, rather than the grain size of the studied films.

3.5. Electrical properties

The as-deposited films dried at a temperature of 100 °C are amorphous and non-conductive. However, the films become conductive after their crystallization through annealing. In case of the film annealed at 285 °C, the Mn⁴⁺ cations are generated (Fig. 6a) and the film is conductive although its XRD pattern does not show any crystalline peaks (Fig. 4). This implies that crystalline nuclei were formed and embedded in the amorphous matrix, but could not be detected by the XRD. For the films annealed at ≥ 300 °C, the crystallized structure was clearly detected by the XRD, and the conductivity of the film increased rapidly with the annealing temperature.

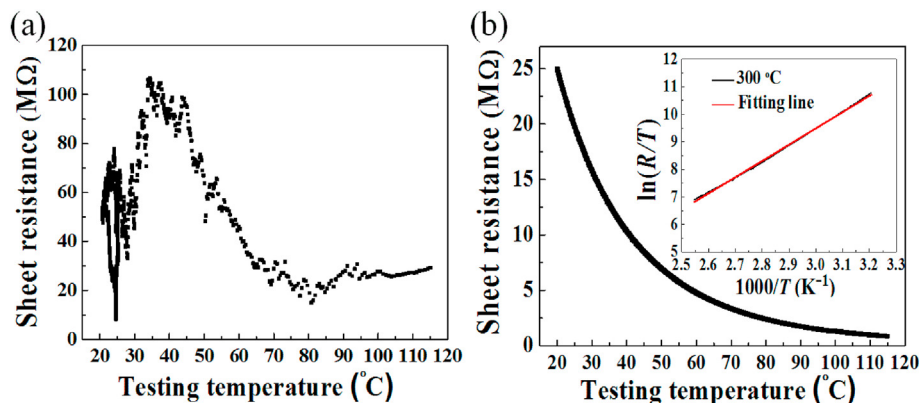


Fig. 7. Resistance–temperature (R–T) curves of films annealed at (a) 285 °C and (b) 300 °C. The insert in Fig. 7b shows the plot of ln(R/T) versus (1000/T) for the film annealed at 300 °C.

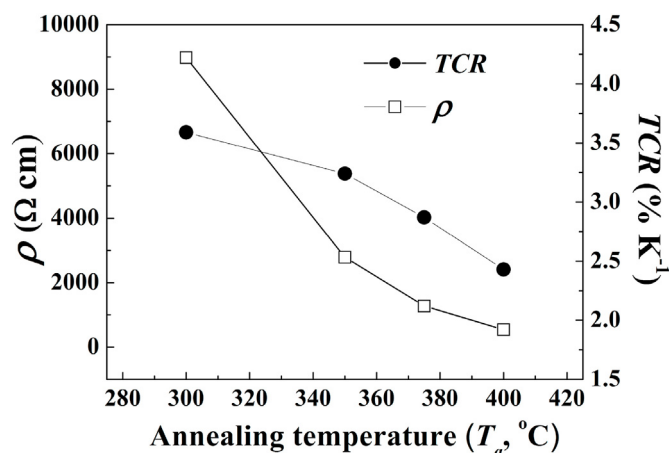


Fig. 8. Dependence on the annealing temperature (T_a) of the RT resistivity (ρ) and absolute temperature coefficient of resistance (TCR) examined on the studied films.

Fig. 7a shows the dependence of the sheet resistance (R) on the testing temperature (T) in the range of $T = 295$ – 368 K (22 – 115 °C) measured by the four-point probe technique for the film annealed at 285 °C. Its R – T curve shows a peculiar behavior: the resistance first increases with the testing temperature, and then decreases; that is, it acts like a mixed positive and negative temperature coefficient material. This phenomenon demonstrates that the film is an unstable semiconductor and is attributed to the incomplete and/or low crystallization. In contrast, the R – T result of the film annealed at 300 °C in Fig. 7b clearly reveals that the sheet resistance decreases with increasing testing temperature, demonstrating a typical NTCR behavior. We therefore emphasize that the critical temperature for obtaining NTCR thin films should be 300 °C. On the other hand, a nearly linear relationship between $\ln R/T$ and the reciprocal of the absolute testing temperature ($1000/T$) is observed for this film (inset in Fig. 7b). The linear relationship between $\ln R/T$ and $1000/T$ can be attributed to the hopping transport mechanism, as described by the Arrhenius model [12,13,18]. A similar result as that shown in Fig. 7b was confirmed for the other films annealed at temperatures of 350 , 375 , and 400 °C.

Fig. 8 presents the change in ρ and absolute TCR at RT, which was examined as a function of the annealing temperature. The ρ and TCR results were derived from the measured sheet resistance (R – T) data [31]. The ρ of the film annealed at $T_a = 285$ °C cannot be determined due to its unstable sheet resistance. However, the result shows $\rho \sim 8980$ Ω cm at $T_a = 300$ °C demonstrates a high conductivity behavior. With the increase in T_a up to 400 °C, the ρ decreases continuously to a minimum value of 541 Ω cm. The tendency of ρ to decrease in Fig. 8 can be attributed to the increase in the carrier concentration rather than the carrier mobility, as shown in Fig. 6b. The resistivity has also been reported to decrease significantly with increasing annealing temperature (300 – 500 °C) for thin oxide Co_3O_4 films obtained by spray pyrolysis in a previous publication [56]. Notably, with $T_a = 350$ °C, a resistivity of 2790 Ω cm can be achieved, which could be interesting for the microbolometer application. Until now, various values of TCR have been reported for bulks, thick films, and thin films of spinel nickel manganite ceramics, and there has been no report of ρ of < 3 kΩ cm at synthesis temperatures below 400 °C. On the other hand, the TCR also decreases with T_a , but is maintained between 2.43 and 3.59 K⁻¹, implying a relatively high temperature-sensitive characteristic of the studied specimens. The TCR values attained in this work are comparable to those of the Mn–Cu–Ni–O films prepared by spin spray [28,29] and metal-organic decomposition [57] methods annealed at temperatures higher than 400 °C.

It has been reported that the aging coefficient ($\Delta R/R$) of nickel manganite films is in the range of 2 – 20% over a period of ~ 500 h at

150 °C in air [58]. In this work, the RT resistance was examined under the same conditions to show the benchmark performance of LFD films annealed at 350 and 400 °C. Both films showed a rapid increase in their sheet resistance in the first 72 h. After that, the resistance increase became less rapid and the system reached a saturation state after 180 and 160 h of aging in the case of films annealed at 350 and 400 °C, respectively. From our aging experiments, it is found that the higher annealing temperature results in a better aging performance. In particular, after 500 h of aging, the $\Delta R/R$ is 6.4% for the film annealed at 350 °C and 5.9% for the one annealed at 400 °C. These aging coefficients are little better compared to those of the undoped nickel manganite films prepared by spin-spraying, annealed at 400 °C in Ar [29].

3.6. Growth mechanism and crystallization

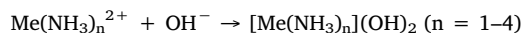
For a better understanding, we propose a possible mechanism of film formation and its crystallization. In the first stage, the possible chemical reaction in the solution associated with the formation of the present films may be similar to the case of hausmannite Mn_3O_4 films deposited by the Chemical bath deposition method [20], which can be represented as



Me^{2+} cations ($\text{Me} = \text{Mn}, \text{Ni}, \text{and Co}$) combine with $\text{NH}_3(\text{aq.})$ to form metal amine complexes, $\text{Me}(\text{NH}_3)_n^{2+}$, via the following reaction:



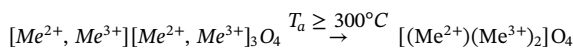
In this case, the substrates were chemically pretreated by Piranha cleaning, which creates $-\text{OH}$ groups on their surface. Therefore, these metal amine complexes are adsorbed onto the substrate with these OH groups, forming a film layer [59]:



When an oxidizing reagent (H_2O_2) is introduced into the system, some of the Me^{2+} ions (Mn^{2+} , Ni^{2+} , and Co^{2+}) are oxidized to Me^{3+} ions, and thus, both Me^{2+} and Me^{3+} ions are simultaneously included in the as-synthesized films, which can be represented as,



Finally, the crystallization (formation of the spinel phase) of films through annealing is possible due to the diffusion and re-arrangement of the Me^{2+} and Me^{3+} cations in the lattice sites:



4. Conclusion

In this study, spinel oxide thin films were successfully produced on Si/SiN_x wafer substrates via an LFD route using aqueous solution. The obtained results indicate that the morphological characteristics of the films depend strongly on the flow speed (α) of the oxidizing solution (H_2O_2) during the synthesis. The films with spherical grains were formed when α was ≤ 100 mL/h, whereas particle agglomeration and precipitation occurred at high H_2O_2 flowing rates ($\alpha \geq 125$ mL/h), degrading the film surface quality. The crystallization of the film was observed to occur at an annealing temperature (T_a) as low as 300 °C, which was attributed to the pre-existence of Mn^{3+} ions in the as-deposited film. Furthermore, the increase in crystallinity with T_a yielded the films highly conductive with a typical NTCR characteristic. Notably, at $T_a \geq 350$ °C, the films possessed an absolute TCR exceeding 2.43% K⁻¹ and a resistivity of < 3 kΩ cm combined with high stability with only 5.9 – 6.4% drift in electrical resistance after 500 h of aging. The presented results suggested that the LFD method benefitted the

synthesis of high-quality spinel oxide thin films for microbolometers.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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