**Characterization of Al-doped Mn-Co-Ni-O NTC thermistor films prepared by the magnetron co-sputtering approach**

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**Abstract**

A serial of Al-doped Mn-Co-Ni-O thermistor thin films were prepared by a magnetron co-sputtering system using an Mn1.4Co1.3Ni0.3 alloy target and an Al target. The composition and electrical properties of the thin films could be well controlled by adjusting the sputtering power of the Al target. It was found that the Mn3+, Mn4+, and Co2+ cations at the octahedral sites of the compact and flat films were gradually replaced by the Al3+ cation during doping. The amount of Al dopant in the compound film was easily adjusted by controlling the sputtering power applied to the doping Al target. The experimental results demonstrate that the NTC characters were found in all films. The optimum point (15W) of Al sputtering power was determined, at which both the maximum material constant *B* value (4112K) and the lowest carrier concentration (2.46×1014 cm-3) was characterized in the film. The significant enhancement of the *B* value for NTC thin films can potentially widen the temperature measurement range for sensing applications.

**Keywords:** Magnetron co-sputtering; Thermistor thin films; Cation distribution; Electrical properties;

**1.Introduction**

Manganese-based transition metal oxides, one of the most classic negative temperature coefficient (NTC) materials, are well suited for use as precise measurement indicators in thermometry [1,2]. The electrical conduction of the manganese (Mn)-based NTC oxides has been determined by the hopping of electrons (charge carriers) between Mn3+ and Mn4+ at the octahedral site [3-5]. The concentration of the charge carriers is determined solely by the doping level, so the resistivity can be tailored to a required value by controlling the doping content and the distribution of multications. In recent decades, the effect of the addition of Al, Mg, Cu, Zn, etc., on the microstructure and electrical properties of Mn-Co-Ni-O ceramics has been systematically studied [6-9]. Indeed, a key trend in the development of discrete thermistor components is building intelligent temperature sensor systems for modern industry control and smart home appliance field applications, which combine sensing elements with communication interface electronics [10-12]. In order to achieve miniaturization and highly integrated characters, the temperature-sensing element usually exists in the form of thermal sensitive thin-film materials. However, we could find few reports on the growth of Mn-based metal oxide films doped with Physical Vapor Deposition (PVD) techniques such as LMBE, PLD, or magnetron sputtering [13-16].

Among these methods, the stoichiometric material and physical properties of films are typically tailored using a target within an optimal ratio and the distribution of multications. Although controlling and monitoring the concentration of doping materials in an Mn-Co-Ni-O system target via traditional ceramic fabrication methods is not complex, stoichiometric films usually contain a deviation compared to the target [17,18].

As a facile and efficient approach to directly fabricate high-quality multicomponent thin films, the co-sputtering process has been well demonstrated. It has been widely used in the preparation of accurate stoichiometric ratio binary compound thin-film materials, such as doped ZnO films [19-21], MgZnO films [22], nickel cermet anode [23], and TiO2:Co thin layers[24].

In this work, a series of Al-doped Mn-Co-Ni-O multicomponent ceramic thin film thermistors were fabricated using magnetron co-sputtering, employing two cathodes with Mn1.4Co1.3Ni0.3 and aluminium sputtering targets. With this simple approach, we found that the aluminium targets’ sputtering power could determine the structure, component, and cation distribution, which further affected the electrical properties of Mn-Co-Ni-Al-O thin films, important for temperature-sensing applications.

**2.Experimental**

2.1 Film fabrication

The serials of Al-doped Mn-Co-Ni-O thin films were deposited on Si (100)/SiO2 substrates by the co-sputtering system using two DC cathodes equipped with Mn1.4Co1.3Ni0.3 alloy target and aluminium target. For the purpose of adjusting the doping content of the Al3+ cation in the thin films, the sputtering power of the Al target was varied in the range of 0 and 20 W (marked as A0, A5, A10, A15, and A20) while the sputtering power of the Mn1.4Co1.3Ni0.3 alloy target was kept constant at optimum 40 W. All the deposition process of Mn-Co-Ni-Al serials films was conducted at the temperature of 150 oC, working pressure of 1 Pa and deposition time of 20 minutes. The substrate platform should be rotated to ensure uniform film deposition. After that, all the films were post-annealed in air at 750 oC for 30 minutes for oxidization and crystalline. The process of films preparation is shown in Fig. 1.



Fig. 1 Schematic of the process for the fabrication of Al-doped Mn-Co-Ni-O films.

2.2 Characterizations and measurements

The structure information of thin-film samples without substrate in this study was characterized using grazing incidence X-ray diffraction (Bruker D8 ADVANCE, Germany) with Cu Kα radiation (=0.15406 nm) in the 2θ range from 25 to 80°. The surface microstructure and thickness of the films were characterized using a scanning electron microscope (LEO 1430VP, Germany) and atomic force microscope (Asylum Research MFP-3D, Britain). X-ray photoelectron spectroscopy (Thermo scientific ESCALAB 250XI; America) was adopted to analyze the cations distribution of Mn, Co, Ni, Al in films. The interdigital electrode Au was deposited on the films by magnetron sputtering in favour of electrical measurements. The electrical resistance was measured at temperatures from -5 to +50 °C using a self-assembled temperature controlling system. The resistivity of films was measured by Hall measurement (Accent HL5500 Hall System, America).

**3.Results and discussions**

3.1 Micromorphology

Fig. 2 shows SEM images of both the surface and cross-section of the Al-doped Mn-Co-Ni-O films prepared by the co-sputtering system and confirms the attainment of co-sputtered films with good smoothness, and no obvious cracks or pores. The thickness of samples gradually increased as the Al sputtering powers increased, which was 70, 110, 130, 155, and 180nm for A0, A5, A10, A15, and A20, respectively. The thickness difference between both films can be attributed to the deposition rate of the target material. This rate was linked to the sputtering yield, defined as the number of ejected atoms per incident argon plasma ions, regulated by the sputtering power [25]. A higher deposition rate resulted from the increasing sputtering power of Al target. Some of the Mn, Co and Ni atoms in the lattice are gradually replaced by Al and more Mn-Co-Ni-Al-O lattices were formed. The added Al would increase the thickness just in the nanometer scale.



Fig. 2 SEM image of the Al-doped Mn-Co-Ni-O thin films (a)A0, (b)A5, (c)A10, (d)A15, (e)A20. Inset: cross-section of SEM.

The quality of co-sputtered films was also confirmed by AFM measurements performed within the silicon substrates (scanned area of 5 x5 μm), as shown in Fig. 3. All the films had protruding coffee bean-like structures consistent with spinel structure surface morphology [11]. The roughness (Rq) of the films was 1.51, 1.12, 1.34, 2.04, and 1.65nm for A0, A5, A10, A15, and A20, respectively. It can be seen from the figure that the roughness of A5 was lower than the others, and A15 was the highest. This was due to the fact that the energy of sputtered particles reaching the surface of the substrate increased during co-sputtering, and the increased surface migration energy of the sputtered particles facilitated nucleation. As the sputtering power increased, the deposition of Al atoms increased as did the atomic stack resulting from the grain growth. However, the fast growth could not support stable grain growth and may have reduced the grain size at an Al sputtering power of 20W, reducing the roughness [26]. Nevertheless, our data confirmed the high quality of the co-sputtered Mn-Co-Ni-Al-O thin films fabricated in this study.



Fig. 3 AFM image of the Al-doped Mn-Co-Ni-O thin films (a)A0, (b)A5, (c)A10, (d)A15, (e)A20.

3.2 Microstructure, Composition, and Cation distribution

Fig. 4 (a) shows the grazing frequency XRD patterns relating to the normalized co-sputtered Al-doped Mn-Co-Ni-O thin films, also illustrating the various sputtering powers of the Al target. The peaks of the films belonged to the spinel phase PDF card No. 23-1237 and priority orientation with (311) crystal orientation. Fig. 4 reveals how the co-sputtered Al was completely diffused into the spinel crystal lattice to form a homogeneous solid solution. All the films had a single polycrystalline spinel structure belonging to the cubic Fdm space group [27] which includes 3, , 4, and symmetry axes. The cations in the tetrahedral sites (T sites) and octahedral sites (O sites) occurred at the inversion point of the and axis, respectively. When the composition changed, these symmetrical point positions did not move, while the O2- anions moved along the 3 symmetry axes. Thus, the side lengths of the tetrahedron and octahedron changed, subsequently resulting in changes in the lattice parameters. A partially enlarged drawing is shown in Fig.4 (b), illustrating that all peak positions positively shifted with increasing Al sputtering power. This occurred due to the Al3+ cation radius (0.053nm) being smaller than those of the substituted Co2+ (0.074nm) and Ni2+ (0.069nm) [28], resulting in a slight decrease in lattice parameter. This outcome demonstrates that the Mn-Co-Ni-Al-O thin films were successfully prepared by co-sputtering and the content of Al cations in the crystal lattice increased with an increase in Al sputtering power.



Fig. 4 (a) XRD patterns of the Al-doped Mn-Co-Ni-O thin films prepared at different Al sputtering powers, (b) the partial enlarged of the XRD pattern.

The composition and distribution of cations in Al-doped Mn-Co-Ni-O films can be studied using XPS. Fig. 5 shows the XPS spectra of Co2p, Ni2p, Al2p, and Mn2p level signals. The spin-orbit splitting of the Co2p state was approximately 15.5eV, consistent with other cobalt-based spinels such as MnCo2O4 [29], Co3O4 [30], and FeCo2O4 [31]. The satellite structures of 2p3/2 provides an effective indication for distinguishing the valence of the Co cation. Referring to MnCo2O4 [29] and Co3O4 [30], the satellite structure related to Co3+ species that should localize at 779.9eV, and the Co2+ species localized at 781.1eV. In order to clearly quantify the variation between different Co cation valence states, the XPS spectra fitting results of Co2p3/2 spectra for all thin films were analyzed, as shown in Fig. 6. The peak intensity was estimated by the peak synthesis procedure, inclusive of Co2+(781.1eV) and Co3+(779.9eV). According to the area of its corresponding peak, the ratios of Co2+/Co3+ were found to be 2.13:1, 2.30:1, 2.01:1, 2.26:1, and 2.17:1 for A0, A5, A10, A15, and A20, respectively.

The Ni2p1/2 and Ni2p3/2 peaks were located at approximately 872.8 and 855.0 eV, respectively, and the spin-orbit split occurred at approximately 17.8 eV. In nickel-containing oxides, the Ni2p3/2 photoemission spectrum showed two obvious peaks labeled as c3d9L and c3d10L, which was a finger print of Ni2+ species. Exactly the same structures had been observed in NiO[32] and Mn1.4Co1.2Ni0.4O4 [33] by other authors. For all the films, Ni element was considered to exhibit bivalence. From Fig. 5c it can be seen that the Al2p peak centred around 73.7eV for A5-A20, and there was no Al element in A0.

The Mn2p1/2 and Mn2p3/2 peaks were centred at 653.9 and 642.4eV, with the splitting of 11.5eV. In order to clearly quantify the variation between different Mn cation valence states, the XPS spectra fitting results of Mn2p3/2 spectra for all thin films were analyzed, as shown in Fig. 6. The peak intensity was estimated by the peak synthesis procedure, inclusive of Mn2+(641.3eV), Mn3+(642.5eV), and Mn4+(644.5eV) [8]. According to the area of its corresponding peak, the proportion of Mn cations with different valence states were calculated and are summarized in Table 1. The ratios of Mn3+/Mn4+ were found to be 2.95:1, 2.90:1, 2.65:1, 2.18:1, and 2.28:1 for A0, A5, A10, A15, and A20, respectively.



Fig. 5 XPS spectra of (a)Co2p, (b)Ni2p, (c)Al2p and (d)Mn2p level signals of Al-doped Mn-Co-Ni-O films with different Al sputtering powers.



Fig. 6 XPS spectra fitting of Co2p3/2 for Al-doped Mn-Co-Ni-O films (a)A0, (b)A5, (c)A10, (d)A15, (e)A20.



Fig. 7 XPS spectra fitting of Mn2p3/2 for Al-doped Mn-Co-Ni-O films (a)A0, (b)A5, (c)A10, (d)A15, (e)A20.

Table 1. the proportion of Mn cations with different valence states.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| sample | Mn2+ (%) | Mn3+ (%) | Mn4+ (%) | Mn3+/Mn4+ |
| A0 | 40.3 | 44.6 | 15.1 | 2.95:1 |
| A5 | 38.3 | 45.9 | 15.8 | 2.90:1 |
| A10 | 32.8 | 48.8 | 18.4 | 2.65:1 |
| A15 | 35.5 | 44.2 | 20.3 | 2.18:1 |
| A20 | 40.2 | 41.6 | 18.2 | 2.28:1 |

The molecular formula of the films, listed in Table 2, were recorded as MnxCoyNizAlwO4+δ, where the subscript conformed to x+y+z+w=3, and their ratio satisfied the atomic content ratio of the XPS measurement result. From Table 2, it is apparent that a wide range of films and their controllable Al content was successfully obtained by controlling the Al target sputtering power in the co-sputtering process. The cation occupancy in the spin structure was based on the model proposed by Yokoyama et al. [34]. In this model, Mn2+ and Co2+ cations prefer to enter tetrahedral sites (T sites) with the preferred order of Mn2+ > Co2+, while the Mn4+, Mn3+, and Ni2+ mainly occupy octahedral sites (O sites) [35]. Moreover, all of the Al3+ cations can be incorporated into octahedral sites. Based on the assumption above and the general spinel form AB2O4, cation distribution in the films could be formulated as,

[HMn2+ICo2+]T[JMn3+KMn4+LCo2+OCo3+MNi2+NAl3+]OO4+δ

where the unknown coefficient could be determined using the following matrix equation:

=

This equation effectively distinguished the variance in the content of different valence Mn ions, thereby retaining the two points after the decimal point of the Mn ion coefficient. The cation distributions of Al-doped Mn-Co-Ni-O films are summarized in Table 2. The Al3+ cation could replace the Mn3+, Mn4+, Co2+ and Co3+ cation at the octahedral sites when the Al target sputtering power was less than 15W. Then, the Al3+ cation would substitute the Ni2+ cation. The ration of Mn3+/Mn4+ was affected by the substitution of the Al3+ cation. It was curious that the Al replacement order on Mn-Co-Ni-O was as follows: Mn>Co>Ni. In this work, the Al first occupied Mn (less than 0.3), then Co (less than 0.3), and finally Ni (less than 0.1). These measurable results demonstrated how easy it was to design the content of Al in Mn-Co-Ni-O system materials by controlling the sputtering power of the Al target.

Table 2. Molecular formula and cation distribution of Al-doped Mn-Co-Ni-O films.

|  |  |  |
| --- | --- | --- |
| sample | Molecular formula | Cation distribution |
| A0 | Mn1.4Co1.3Ni0.3O4+δ | [0.56Mn2+0.44Co2+]T[0.62Mn3+0.22Mn4+0.44Co2+0.42Co3+0.3Ni2+]OO4+δ |
| A5 | Mn1.2Co1.2Ni0.3Al0.3O4+δ | [0.46Mn2+0.54Co2+]T[0.55Mn3+0.19Mn4+0.30Co2+ 0.36Co3+0.3Ni2+0.3Al3+]OO4+δ |
| A10 | Mn1.1Co1.1Ni0.3Al0.5O4+δ | [0.36Mn2+0.64Co2+]T[0.54Mn3+0.20Mn4+0.10Co2+ 0.36Co3+0.3Ni2+0.5Al3+]OO4+δ |
| A15 | Mn1.1Co1.0Ni0.3Al0.6O4+δ | [0.39Mn2+0.61Co2+]T[0.49Mn3+0.22Mn4+0.08Co2+ 0.31Co3+0.3Ni2+0.6Al3+]OO4+δ |
| A20 | Mn1.1Co1.0Ni0.2Al0.7O4+δ | [0.44Mn2+0.56Co2+]T[0.46Mn3+0.20Mn4+0.13Co2+ 0.31Co3+0.2Ni2+0.7Al3+]OO4+δ |

3.3 Electrical properties

Fig.8 (a) plots the resistance (*R*) of several MCN films and Al-doped Mn-Co-Ni-O film as a function of temperature (T) in the temperature range of -5 to +50°C. It illustrates that all of the sample resistance decreased exponentially with increasing temperature, revealing the characteristics of NTC. The resistance characteristics of the films could be described the generalized expression for small polaron hopping model as following equation [5]: R = CT*α*exp(Tc/T)*p*, where R is the resistance at corresponding operating temperature T, C is a constant related to temperature, Tc is the characteristic temperature, for nearest-neighbor hopping (NNH) model, *α* = *p* = 1, while for variable range hopping (VRH) model 0.25 < *p* = *α*/2 < 1. It is possible to elucidate the electron conduction mechanism by determining *p* from the slop of the plots of ln(*W*) versus ln(T) for films as shown. The *W* can be described by [36]:

In this case, the obtained data are analyzed by linear least-squares methods. The slope of the fitting line gives the value of the corresponding *p*. Fig.8(c) shows the *p* values were 1.049, 0.986, 1.078, 1.164 and 1.120 for A0, A5, A10, A15, and A20, respectively. All the values of *p* were close to 1, which indicated that the hopping type of the films fits to NNH model.

Therefore, the electrical resistance in bulk thin ﬁlms are better described by a nearest-neighbour hopping mechanism, given by, where A is the resistance of the device at inﬁnite temperature, and *B* is the so-called material constant of a thermistor. According to this equation, the *B* value can be calculated by the equation:, where R1 and R2 correspond to the resistances measured at T1 and T2, respectively [37]. Usually, the *B* value was calculated using the resistance of 25°C and 50°C, recorded as *B25/50*. Fig.8 (b) shows the relationship between Ln(R) and the reciprocal of the absolute temperature (1/T) for all films. The *B25/50* value of the films were 3418, 3579, 3659, 4112, and 3971K for A0, A5, A10, A15, and A20, respectively. Increasing at Al sputtering power values lower than 15W, it then decreased. This phenomenon can be explained by the electronic transport in Mn-based spinel oxides, that is, the hopping of small polarons between Mn3+ and Mn4+. The *B* value increased with the decreased Mn3+/Mn4+ ratio, which is consistent with the reported literature [4,17]. From Fig. 8, it can be seen that the resistance value at room-temperature became higher with the increasing Al3+ content, resulting from the increased thickness of the films. In order to avoid thickness interference, the resistivity of the film was measured to further explain the effect of Al doping on the electrical properties of the films. The resistivity (*ρ*), and carrier concentration (nc) of the films were measured using the Hall effect measurement system at 303K, summarized in Table 3. It can be seen that the resistivity increased with the higher Al content. In addition, both the lowest nc (2.46×1014 cm-3) and the highest B (4112 K) belonged to the film with an Al sputtering power of 15W. The corresponding change relationship between nc and *B* was due to both being temperature independent and was determined solely by the doping level.



Fig. 8 (a) relationship between electrical resistance and temperature. (b) Ln(R) versus 1000/T and (c)ln*W* versus lnT plots for Al-doped Mn-Co-Ni-O films.

Table 3. resistivity, resistance, carrier concentration and the *B25/50* value of Al-doped Mn-Co-Ni-O films measured at 303K.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| sample | Resistivity  (Ω cm) | Resistance  (kΩ) | carrier concentration (cm-3) | *B25/50*  (K) |
| A0 | 6.84×101 | 42.8 | 1.68×1016 | 3418 |
| A5 | 2.17×102 | 48.8 | 1.84×1015 | 3579 |
| A10 | 6.33×102 | 59 | 8.24×1014 | 3659 |
| A15 | 7.00×102 | 88 | 2.46×1014 | 4112 |
| A20 | 2.15×103 | 133.7 | 7.10×1014 | 3971 |

**4.Conclusions**

In this study, smooth-surfaced Al-doped Mn-Co-Ni-O thermistor thin films were successfully deposited, without an impurity phase, by the magnetron co-sputtering approach. The NTC characters existed in all films. In the multicomponent spinel Mn-Co-Ni-Al-O, the Al first occupied Mn (less than 0.3), then Co (less than 0.3), and finally Ni (less than 0.1), demonstrating that the composition and the Al ratio of the Mn-Co-Ni-O system thin films could be well controlled by adjusting the sputtering power of the Al target. The resistivity of the films grew with increasing Al-content, which is in agreement with the expectation of a wider temperature range for sensing applications. The maximum material constant *B* value (4112K) and the lowest carrier concentration (2.46×1014 cm-3) of the film were achieved when the Al target sputtering power was 15W. Both parameters were independent of temperature and were dominated by the doping level.

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