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FABRICATION OF $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ $(0 \leq x \leq 0.2)$ THIN FILMS ON $LaAlO_3$ SUBSTRATES VIA CHEMICAL SOLUTION DEPOSITION

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Abstract. Epitaxial $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ $(0 \leq x \leq 0.2)$ thin films are fabricated successfully on $LaAlO_3$ (LAO) (100) substrates using chemical solution deposition method. The results reveal that with the increase of the Ni-doping content, the X-ray diffraction intensity ratio of $I_{(111)}/I_{(200)}$ increases, whereas both the grain size and the roughness decrease. The magnetic and transport measurements show that it is effective to tune the MR effects via Ni doping at Mn-sites.

1. INTRODUCTION

Since the discovery of colossal magnetoresistance (CMR) effect in the perovskite manganites $La_{1-x}A_xMnO_3$, where A is alkaline–earth–metal or alkali–metal element or Pb, these manganites have been extensively investigated in the past years not only because of their scientific interest but also of their potential applications in various devices such as magnetic field sensors and hard disk read heads [1-3]. Most of these studies have focused on the divalent alkaline–earth–metal doping at A site, such as Ca, Sr, Ba, or Pb [4-6]. There have fewer studies about monovalent alkali–metal doping at A site. Compared to the divalent dopants, as to the monovalent doping, such as sodium dopants, there have some advantages: first, in theory, the same number of Mn^{4+} produced by the usual divalent cation doping can be obtained with one half concentration of monovalent dopant. Besides, the cationic radius of the Na^+ (0.139 nm) is very close to La^{3+} (0.136 nm); hence one may introduce a large amount of charge carrier without appreciable lattice distortions and achieve the maximum integral transfer for the double exchange (DE) at about $x = 0.16$ [7-9]. Additionally, some studies have been investigated about doping at Mn sites with various elements, such as Cu, Al, Fe, Ga, Ti, Sn, Co, Ni, or Cr, and the results show that it is possible to tune the metal-insulator (M-I) transition and the MR effects via the doping of the Mn-sites [10-14].

It is well known that many practical applications require that the material should be in the form of films. As for the fabrication of CMR films, compared with the physical methods, such as pulse laser deposition (PLD) and magnetron sputtering (MS) technique, the chemical solution routes for the preparation of thin films have some advantages, such as precise control over the stoichiometry and being easier to fabricate large-area films. Moreover, the chemical solution deposition (CSD) technology is simple and low-cost [15-17]. As far as we know, there have relatively few works concerning about preparation of alkali-metal doped CMR thin films [18], especially, via CSD methods. In our previous works [19], it is found that the bulk Na-doped manganites have appreciable MR near the room temperature, which is necessary for the applications. In this paper,

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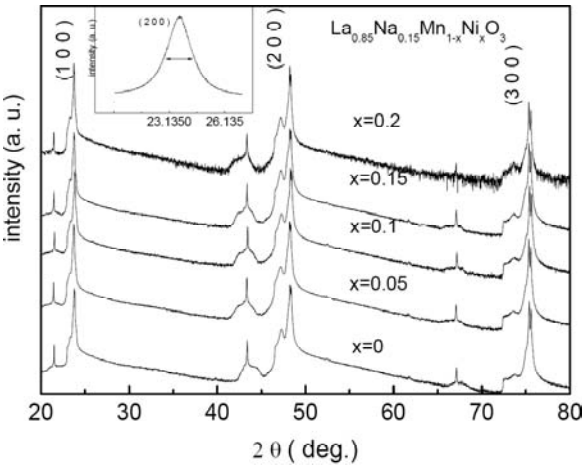


Fig. 1. XRD θ-2θ patterns of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films. The inset is the amplification of the (200) reflection peak.

the preparation of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ ($0 \le x \le 0.2$) epitaxial thin films using CSD method on LAO (100) substrates and their transport properties are reported.

2. EXPERIMENTAL PROCEDURES

$La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ ($0 \le x \le 0.2$) thin films were fabricated on LAO (100) single crystal substrates by propionate route. The propionate solutions were synthesized from commercially available chemicals. In brief, stoichiometric amounts of $La(CH_3COO)_3{\cdot}6H_2O$, $Na(CH_3COO){\cdot}0.5H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$ and $Mn(CH_3COO)_2{\cdot}6H_2O$ were dissolved in propionic acid and distilled off the liberated acetic acid. After removal of the acetic acid and a great portion of the propionic acid the solutions were diluted by n-butanol and propionic acid to give a 0.2 M in propionic acid/butanol 2:1 [20]. These precursor solutions were insensitive to moisture and can be handled in ambient atmosphere. Before the process of depositing, these solutions were filtered, and the substrates were cleaned by an ultrasonic cleaner using acetone, ethanol and water successively. Deposition of these films was carried out by a spin-coater using 500 rev./min for 5 s, followed by 4000 rev./min for 60 s. The as-deposited films were pyrolyzed at 300 °C for 30 min to dry the films. The dried films were finally annealed at 800 °C for 2 hours under flowing oxygen atmosphere in a quartz tubular furnace. In order to obtain the films with the desired thickness, the above spin coating, drying and annealing processes were repeated several times.

A Philips X'pert PRO X-ray diffractometer (XRD), a Sirion 200 field emission scan electron microscope (FE-SEM) by FEI Company and a Park Scientific Instruments designed Autoprobe CP type atomic force microscope (AFM) were used to characterize the crystallization quality, thickness and the microstructure of the films, respectively. The thickness of all the studied films determined by the cross-section of FE-SEM was about 300 nm. The temperature dependence of the resistance under the applied field $H = 0$ and 0.5 T was measured by the standard four-probe method in the temperature range from 30 to 300K obtained by means of using a closed-cycle He refrigerator.

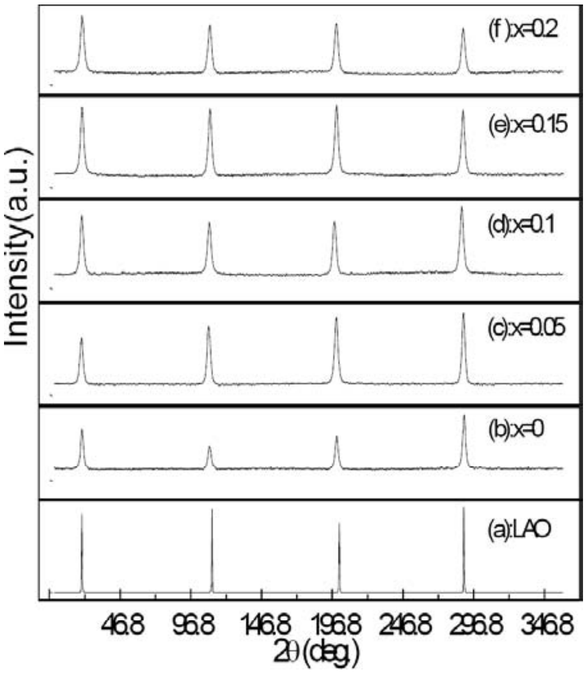
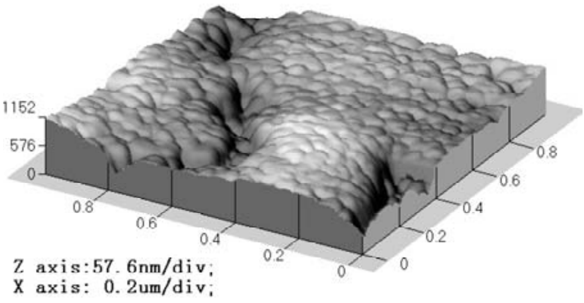


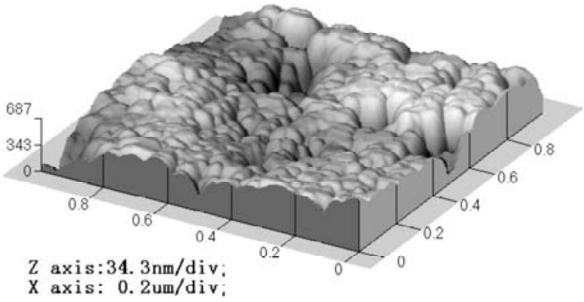
Fig. 2. The XRD in-plane φ scans for LAO (220) and $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ (220).

3. RESULTS AND DISCUSSION

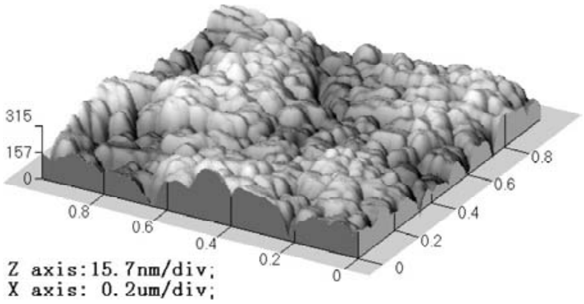
Fig. 1 shows the θ-2θ XRD pattern of the $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ ($0 \le x \le 0.2$) films on LAO substrates. There only exist (h00) peaks attributed to $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films besides (h00) peaks of the LAO substrate, implying that these films are a-axis oriented. The inset of Fig. 1 is one of the typical rocking curve results of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ (200) peaks; all the others are similar to this result. It shows that the full width at half maximum (FWHM) is only about 1.6°-1.9°, indicating that the out-of-plane orientation of these films is rather good. The in-plane φ scans of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ (220) thin films are shown in Fig. 2, which indicates that these films are of the four-fold symmetry and grow on the LAO substrates in the cube-on-cube method. The value of FWHM of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ (220) is 2.6°,



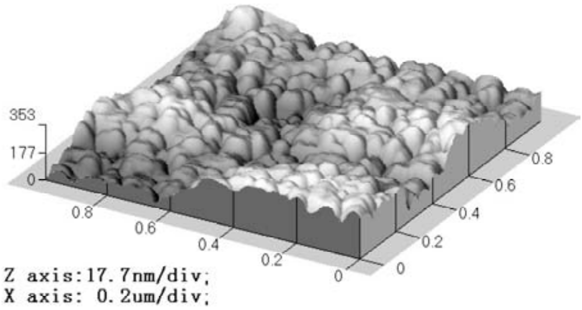
(a) x = 0



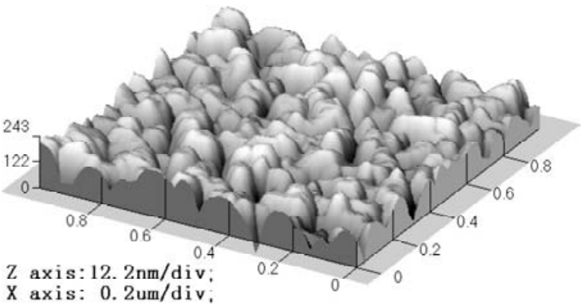
(b) x = 0.05



(c) x = 0.1



(d) x = 0.15



(e) x = 0.2

Fig. 3. The AFM images of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films.

2.7°, 2.9°, 2.8°, 3.1° for $x = 0, 0.05, 0.1, 0.15, 0.2$, respectively, which indicates the in-plane orientations deteriorate with increase of the Ni content. Considering the FWHM (~ 0.8°) of LAO (220), the value of FWHM of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ (220) indicates that both in-plane and out-of-plane orientations of the film are quite good [15].

The AFM images of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films on $LaAlO_3$ are shown in Fig. 3. The average grain sizes determined from AFM are about 60 nm for all the $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films, which indicates the grain size unchanged with increasing of the Ni content. From the AFM images, it can be seen that the grain growth is in the form of three-dimension (3D) island resulting in granular structure. Additionally, there exist some evident grooves embedded for $x = 0$ and $x = 0.05$, which may be related to the volatility of sodium element. The roughness obtained in the range of 1×1 mm^2 is 17 nm, 14 nm, 7 nm, 7 nm, and 5 nm for $x = 0$, $x = 0.05$, $x = 0.1$, $x = 0.15$, and $x = 0.2$, respectively, which indicates that the films are rather smooth when $x>0.05$. From the above results it can be suggested that the Ni-doping at Mn-site can depress the roughness.

The temperature dependence of the resistivity at $H = 0$ and 0.5 T perpendicular to the film surfaces is shown in Fig. 4. At zero field, the M-I transition, T_p, obtained from the maximum resistivity, is 330K, 237K, and 207K for $x = 0$, $x = 0.05$, and $x = 0.1$, respectively. However, for the sample $x = 0.15$, and $x = 0.2$, there have no M-I transition in the measured temperature range, and exhibits the insulting behavior in the whole measured temperature range. The resistivity at $H = 0$ for $x = 0$ is rather low, $4.9\times 10^{-2}\ \Omega\cdot$cm, similar to that of laser deposition [18]. Additionally, the resistivity increases with the increase of Ni content. As for the variation of the transport properties, it is suggested to be related to the destruction of Mn^{3+}-O-Mn^{4+} networks due to the substitution of Ni ions for Mn ions. That is to say, with the increase of Ni content, the DE is depressed resulting in the decrease of the M-I transition temperature and the enhancement of the resistivity.

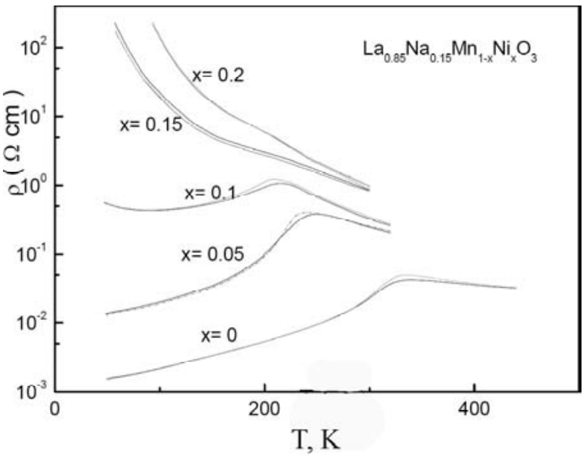


Fig. 4. The temperature dependence of the resistivity for of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films under H = 0 and 0.5 T.

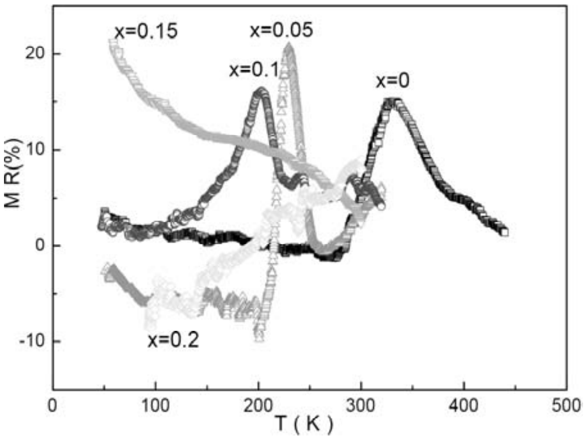


Fig. 5. The temperature dependence of MR under 0.5 T for of $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ films.

Additionally, the grain boundary effects cannot be neglected.

Fig. 5 is the temperature dependence of magnetoresitance [MR, defined as $(\rho_{H\text{-}}\rho_0)/\ \rho_0\times100\%$, where ρ_0, ρ_H is the resistivity under H = 0 and 0.5 T, respectively] at H = 0.5 T for the x = 0, x = 0.05, and x = 0.1, respectively. It can be seen that obvious peaks, 15% at 329K, 21% at 229K, and 16% at 202K for x = 0, x = 0.05, and x = 0.1, respectively, these peaks are in the vicinity of corresponding T_p. Moreover, it has no MR peaks for x = 0.15, and x = 0.2. Additionally, for the x= 0.15, it can be observed from Fig. 5 that the value of MR increases with the decrease of temperature and is 2.3% and 20% at 300K, 60K, respectively. Inversely, for the x = 0.15, the value of MR increases with the increase of temperature and is 8% and -8% at 300K, 94K, respectively.

4. CONCLUSION

In conclusion, $La_{0.85}Na_{0.15}Mn_{1-x}Ni_xO_3$ epitaxial thin films were successfully fabricated on LAO (100) substrates by CSD method. The results showed that in-plane and out-of-plane orientations are quite good, the roughness decreased with the increase of Ni content, the transport measurements revealed that it was effective to tune the MR effects via Ni doping at Mn-sites, $La_{0.85}Na_{0.15}MnO_3$ film on $LaAlO_3$ have a good conductivity by CSD.

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