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Preparation of $La_{0.85}Na_{0.15}MnO_3$ Films by Sol-gel Method

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ABSTRACT

All a-axis oriented $La_{0.85}Na_{0.15}MnO_3$(LNMO) films are fabricated successfully on $LaAlO_3$ (LAO) (100) substrates by sol-gel method. The results of the θ-2θ XRD pattern, rocking curve and φ scan reveal that both in-plane and out-of-plane orientations of the film are quite good. The transport measurements show that the resistivity of the films by sol-gel is very close to that by PLD. It is said that sol-gel method can substitute vacuum methods fabricating LNMO/LAO films.

Keywords: Magnetoresistance; Thin film; Sol-gel

I. INTRODUCTION

The perovskite manganites colossal magnetoresistance materials have attracted great interest due to their potential applications and rich physical connotations. In the $La_{1-x}A_xMnO_3$ system, most studies focus on doping divalent alkaline earth metals at the A-site, such as Ca, Sr, Ba, or Pb [1-3]. There is a little research on doping of monovalent alkali metals, on A-site doping of monovalent alkali metals, such as Li, Na, K, Rb, etc. [4-5]. Compared to divalent doping, monovalent alkali metals such as Na doping have the following advantages:

1.1 Low doping concentration:
In theory, at the same doping concentration, the number of Mn^{4+} produced by monovalent doping is twice that of divalent doping, which means that monovalent ions only need half of the doping concentration to reach the required number of Mn^{4+} for divalent doping.

1.2 The doping Ionic radius is close to:
The Ionic radius of Na^+(0.139nm) is very close to that of La^{3+}(0.136nm), so the lattice effect introduced by doping can be ignored.

1.3 Ion substitution disorder small:
Due to the fact that less unit price doping can meet the doping requirements, theory suggests that optimal doping can be achieved when x=0.16, so the substitution disorder introduced by doping is small.

1.4 It has a significant MR effect near room temperature [6].

As is well known, thin film materials are widely used in materials and are one of the main application forms of materials [7]. The main methods of preparing thin films are physical methods, such as Pulsed laser deposition, magnetron sputtering, etc. These methods can prepare high-quality thin films. However, its production area is limited and requires operation in a vacuum chamber, resulting in high costs. Sol-gel method can prepare large area thin films, but its precursor colloids are difficult to prepare. Compared with the chemical vapor phase method, the Sol-gel method is safer for preparing thin films [8].

$La_{0.85}Na_{0.15}MnO_3$(LNMO) has a higher Curie temperature than room temperature, indicating that its MR effect can be utilized at room temperature. At present, one of the main problems in the application of colossal magnetoresistive materials is that under small magnetic fields, the magnetic resistance near room temperature is too small to be practical. Therefore, it is very important to study the low field magnetoresistance effect of LNMO.
In this article, we prepared LNMO thin films on single crystal $LaAlO_3$ sheets using a sol-gel method, and studied the orientation and magnetoelectric transport properties of the films.

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II. EXPERIMENTAL PROCESS

2.1 Selection of substrate

$LaAlO_3$ (1 0 0) single crystals were chosen as substrates.

2.2 Preparation of precursor colloids

The solutions of $La_{0.85}Na_{0.15}MnO_3$(LNMO) were synthesized from commercially available chemicals. Calculate and weigh the weights of $La(NO_3)_3 \cdot 6H_2O$, $Na(CH_3COO) \cdot 0.5H_2O$ and $Mn(CH_3COO)_2 \cdot 6H_2O$ (with a purity higher than 99%) according to the chemical ratio of 0.85:0.15:1, and completely dissolve them in a water/ethanol solution containing citric acid (volume ratio 1:9). The chemical ratio of metal ions and citric acid ions is 1:2. Mix these three solutions together and stir until they are completely dissolved. Add polyethylene glycol with a molecular weight of 20000 as a surfactant to prevent the chelation and aggregation of colloidal particles [9]. The chemical reagents used here require analytical purity. Then dilute the colloid concentration to 0.2-0.3M with a water/ethanol solution (volume ratio of 1:9). Finally, the solution was prepared with a pore size of 0.2 μM filter filtration.

2.3 Substrate cleaning

The substrates were ultrasonically cleaned using acetone, ethanol and water sequentially.

2.4 Glue throwing

Deposition of LNMO was carried out by a spin-coater at 500 rpm for 5 s, followed by 3000 rpm for 60 s. The as-deposited films were dried at 300℃ for 30 min. The dried films were finally annealed at 800℃ or 900℃ for 2 h under flowing oxygen atmosphere in a quartz tube furnace. In order to obtain the film with the desired thickness, the above spin coating, drying and annealing processes were repeated several times.

2.5 Sintering

Place the deposited thin film in a quartz tube and then place it in a tube furnace. Inject flowing oxygen and keep it warm for 30 minutes at 300 ℃, then anneal at 800 ℃ for 2 hours, and finally cool down with the furnace. Repeated throwing and sintering can achieve the required thickness of the film.

A Philips X'pert PRO X-ray diffractormeter (XRD), were used to characterize the crystallization quality.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.

III. RESULTS AND DISCUSSION

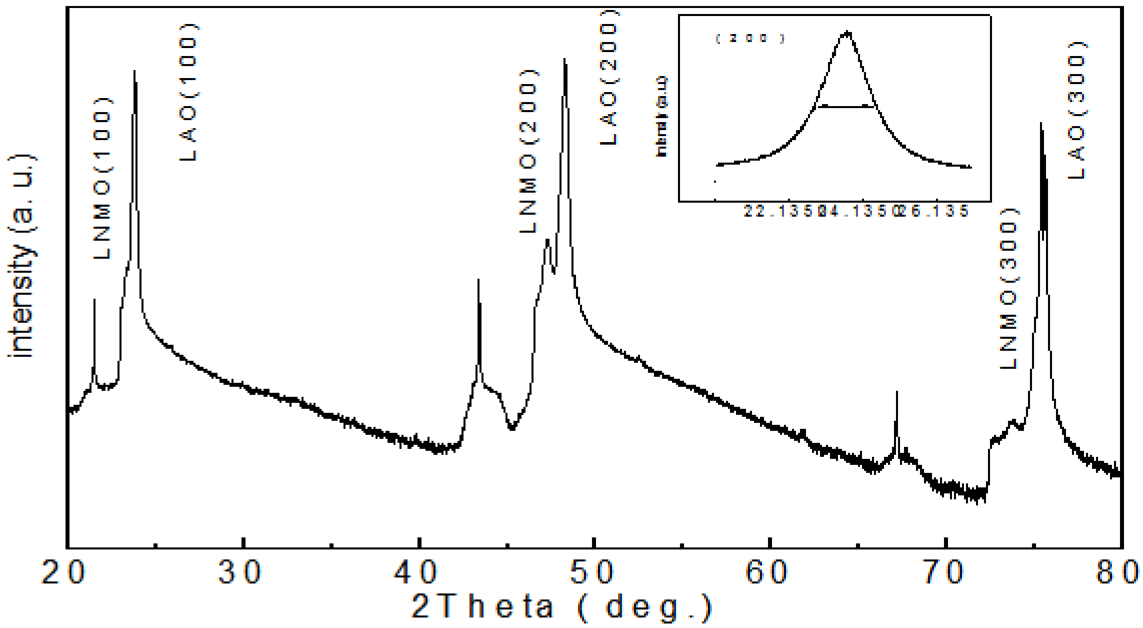

Figure1 XRD diffraction pattern of LNMO / $LaAlO_3$ films.

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The inset is the amplification of the (200) reflection peak.

Figure 1 shows the XRD diffraction pattern of LNMO thin film on $LaAlO_3$ substrates. From the figure, it can be seen that the film has a perovskite pseudocubic structure, and no impurity peaks other than LNMO were found, indicating that the film is a pure phase. The three strongest peaks are the (h00) diffraction peak of single crystal LAO. Because the lattice constant is very close, the (h00) diffraction peak of LNMO film is close to the peak of the substrate LAO, and the film grows along the (h00) direction of the substrate. Among them, (200) is the strongest, (300) is second, and (100) is the weakest; No other diffraction peaks other than (h00) appeared. It indicates that the orientation of the thin film is high, and it grows in the complete (h00) direction with good a-axis orientation.

To further determine the epitaxial state of the thin film, we measured the rocking curve of the (200) diffraction peak of the LNMO thin film - out of plane orientation and the Phi scan of the (220) diffraction peak - in plane orientation.

The illustration in Figure 1 shows the rocking curve of the diffraction peak of LNMO/LAO thin film (200), with a fixed value of $2\theta = 47.4^{o}$. The full width of half maximum (FWHM) of the diffraction peak is 0.9^{o}. FWHM is an important index to measure the epitaxial performance of thin films. For thin films prepared by chemical methods, when FWHM is less than 1.0^{o}, they can be considered to have good epitaxial growth. The results indicate that the film we prepared has a good out of plane orientation.

Figure 2 shows the Phi scan results of the diffraction peaks of LNMO/LAO thin film (220). It can be seen that the film shows good quadruple symmetry, which is completely corresponding to LAO single crystal, indicating that it is a cubic cubic growth mode. From the FWHM results of Phi scanning, it can be seen that the FWHM results of LNMO thin film in Figure 2 (b) are 2.6^{o}, which shows better in-plane and out of plane orientation compared to 0.8o of LAO single crystal in Figure 2 (a) [10].

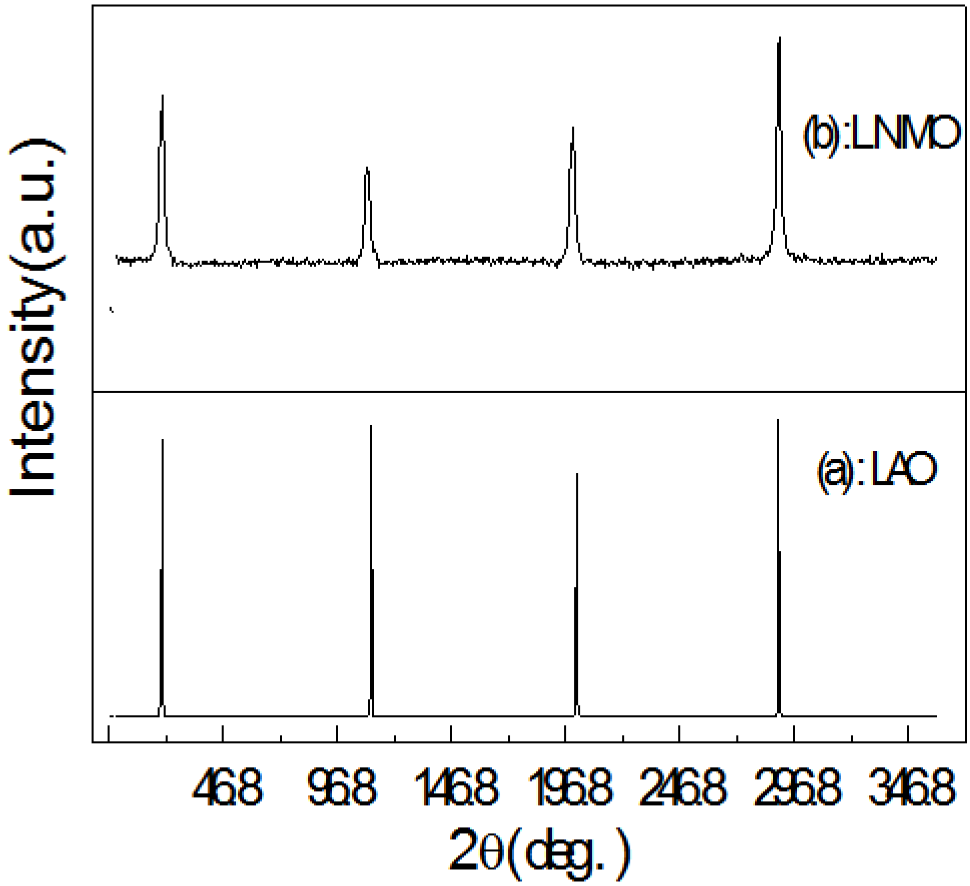

Figure 2 The Phi scan results of the diffraction peaks of LNMO/LAO thin film (220)

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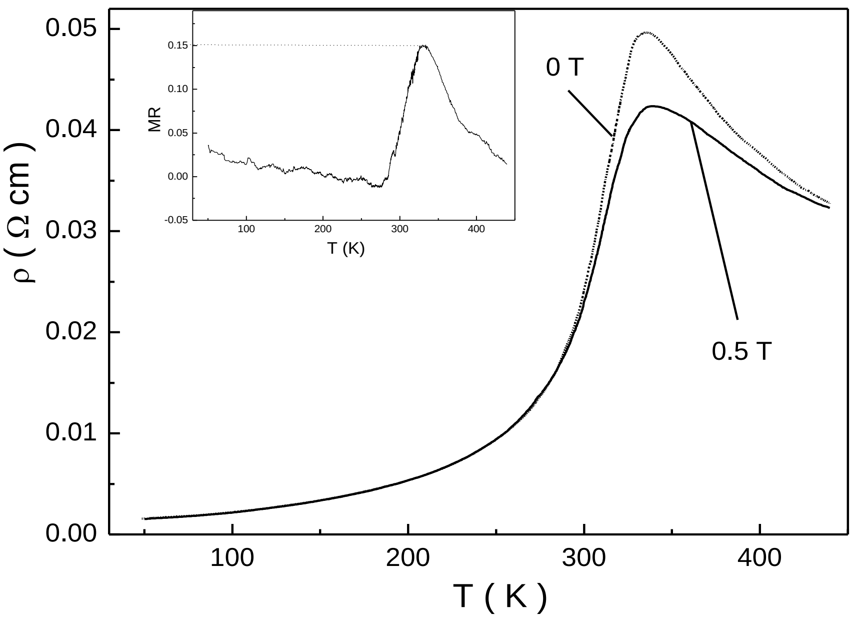

Figure 3 The temperature dependence of the resistivity for of LNMO/LAO under H = 0 and 0.5T. The inset is MR Curve of variation with temperature the amplification of the (200) reflection peak.

Measure the resistance (R) - temperature (T) curves of LNMO/LAO thin films under different magnetic fields using the four lead method, and calculate the resistivity(ρ). The relationship between the change in temperature (T) and the change in temperature (T) is shown in Figure 3. The dashed line in the figure represents the resistivity under zero field, while the solid line represents the resistivity under an applied magnetic field of 0.5T, with a temperature range from 50K to 440K. The metal insulator transition temperature (TMI) of LNMO thin film under zero field is 330 K. The resistivity below TMI increases with temperature, indicating metallic behavior, while the resistivity above TMI decreases with temperature, indicating insulation behavior.

The inset of figure 3 illustrates magnetoresistive MR（$(\rho_H-\rho_0)/\rho_0 \times 100\%$) Curve of variation with temperature. Under an external magnetic field of 0.5T, a clear peak can be observed with a large MR, reaching up to 15% at 329K, near the metal insulator transition temperature.

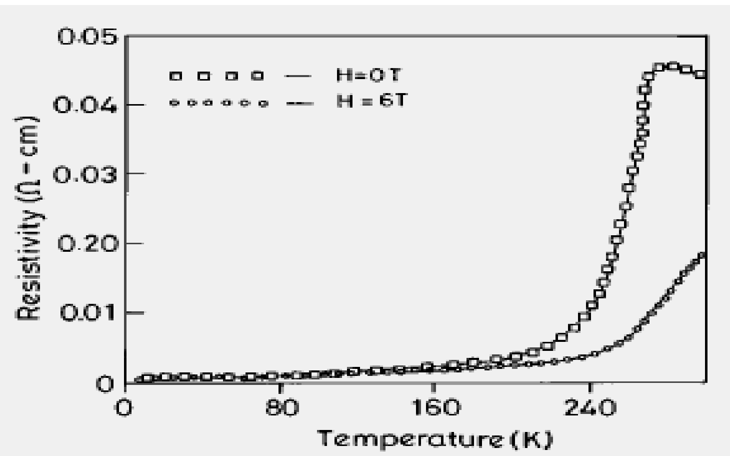

Figure 4. The temperature dependence of MR for of $La_{0.83}Na_{0.11}MnO_3$/LAO films.

Figure 4 shows M Sahana et al. used the PLD method to deposit thin films on LAO single crystals and first conducted research on $La_{0.83}Na_{0.11}MnO_3$ thin films [11].

By comparing Figures 3 and 4, it was found that the resistivity of the LNMO thin film prepared by sol-gel method was very low, with a maximum value of ρ= 4.9 × 10^{-2} Ω• cm at T_{MI}, which is very close to the resistivity of $La_{0.83}Na_{0.11}MnO_3$ thin film prepared by PLD method. This indicates that the sol-gel method can replace the vacuum method to prepare LNMO/LAO thin films.

IV. CONCLUSION

Oriented LNMO/LAO thin films were successfully prepared on $LaAlO_3$ (100) single crystal using a sol-gel method, with good in-plane and out of plane orientation. The transport results show that the resistivity of the thin film prepared by the sol-gel method is very close to that obtained by the PLD method. This indicates that the sol-gel method can replace the vacuum method to prepare LNMO/LAO thin films.

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