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Preparation of $LaMnO_3$ and $La_{0.85}MnO_3$ Films by Sol-gel Method

Liu Sheng-Man[1,*], Li Juan[2], Wang Ting-Tai[1], Qin He[1], Jin Wen-Tao[1], Li Li-Ping[1]

(Zhongyuan University of Technology, Zhengzhou 450007, PR China)
[1]College of Physics and Optoelectronic Engineering, Zhongyuan University of Technology, Zhengzhou 450007, PR China
[2]Archives, Zhongyuan University of Technology, Zhengzhou 450007, PR China

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ABSTRACT
$LaMnO_3$ and $La_{0.85}MnO_3$ films are fabricated successfully on Si (100) substrates by sol-gel method, $LaMnO_3$ films with (h00) orientation and $La_{0.85}MnO_3$ films with random orientation. The results show that temperature and atmosphere can obviously affect the orientation of $LaMnO_3$ films. Moreover, it is found there exist an insulator-metal transition in the $LaMnO_3$ films, which can be attributed to the oxygen excess. La-deficient can improve crystallization quality and the microstructure of the film. For the $La_{0.85}MnO_3$ films, show an obvious low field magnetoresistance (LFMR), which is beneficial to practice application.
Keywords: Magnetoresistance; Thin film; Sol-gel

I. INTRODUCTION

Since the colossal magnetoresistance (CMR) effect in the perovskite doped manganese oxides $R_{1-x}A_xMnO_3$ (R is a trivalent rare-earth element such as La, Nd, or Pr, A is a divalent dopant such as Ca, Sr, Ba, or Pb) is discovered, it has been extensively investigated in past few decades not only because of its scientific interest and but also of its potential applications in various devices such as magnetic field sensors or hard disk read heads [1-4]. It is well known that many practical applications require that the material should be in the form of film. At present, although CMR films can be successfully grown on various single substrates such as $SrTiO_3$ (STO), $LaAlO_3$(LAO)

or MgO [5-7], the growth of CMR films on the technologically viable substrates such as Si, Ge, InAs or GaAs is essential for the future commercial applications because these substrates are main

microelectronic materials. In addition, the low-field magnetoresistance (LFMR) is also prerequisite for the application of CMR materials. However, for single crystal or highly orientated CMR films, MR effect appears only in the vicinity of the metal–insulator (I-M) transition temperature and at high magnetic fields with the order of magnitude of several tesla, which seriously limits their practical applications. Since Li et al., find that the polycrystalline perovskite manganite films can demonstrate an enhanced MR, which is mainly dominated by spin-dependent

scattering of polarized electrons at the grain boundaries (GBs) [8], a lots of references on the LFMR and temperature independent MR properties in the manganites are reported [9-10]. The La-deficient perovskite manganite compositions $La1\text{-}xMnO_3$ exhibit magnetic and electrical properties very similar to that of the divalent cation doped [11].

As is well known, the fabrication of CMR films is usually focused on the physical methods, such as pulse laser deposition (PLD) or magnetron sputtering (MS) technique. Compared with physical methods, the chemical solution routes for the preparation of thin films have some advantages, such as precise control over the stoichiometry on substrate over a large area. Moreover, the sol-gel technology is simple and low-cost. Therefore, recently, the fabrication of CMR films using sol-gel method attracts one's attention [12-14].

In this paper, the preparation of $LaMnO_3$ and La-deficient perovskite manganite $La_{0.85}MnO_3$ polycrystalline thin films using sol-gel method on Si (100) substrates and their transport properties are reported. Herein, the reason why we select Si as substrates is that Si is commonly used in the semiconductor industry and can be commercially

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obtained, which can further lower the fabrication cost.

II. EXPERIMENTAL PROCESS

2.1 Selection of substrate

Si (1 0 0) single crystals were chosen as substrates.

2.2 Preparation of precursor colloids

The solutions of $LaMnO_3$ and $La_{0.85}MnO_3$ were synthesized from commercially available chemicals. Calculate and weigh the weights of $La(NO_3)_3 \cdot 6H_2O$, and $Mn(CH_3COO)_2 \cdot 6H_2O$ (with a purity higher than 99%) according to the chemical ratio of 1:1 and 0.85:1, 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 $LaMnO_3$ and $La_{0.85}MnO_3$ were carried out by a spin-coater at 500 rpm for 5 s, followed by 3000 rpm for 60 s.

2.5 Sintering

Place the deposited thin films 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 600, 700, 800, 900 ℃ 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) and Park Scientific Instruments designed Autoprobe CP type atomic force micrograph (AFM) were used to characterize the crystallization quality and the microstructure of the film. The temperature dependence of the resistance under applied field H=0, 0.1 and 0.5 T was measured by the standard four-probe method in the temperature range from 30 to 300 K obtained by means of a cryogenic refrigeration equipment. The magnetoresistance (MR) was defined as $MR=[(R_0-R_H)/R_H]\times100\%$, where R_0 and R_H were the resistance at zero field and applied field, respectively.

III. RESULTS AND DISCUSSION

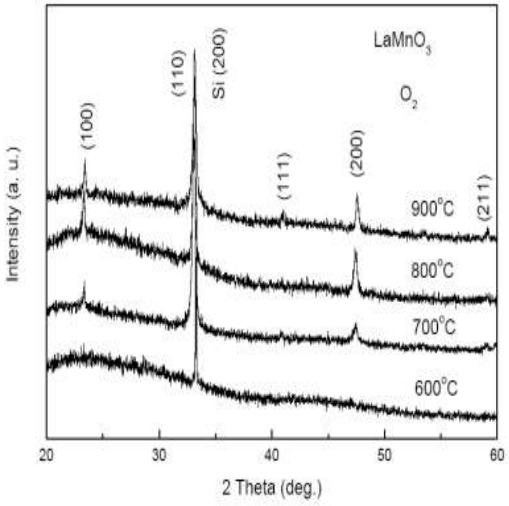

Figure 1 XRD diffraction pattern of LaMnO3/Si films are annealed at 600, 700, 800, 900℃ in flowing oxygen.

The standard θ-2θ XRD patterns for the $LaMnO_3$ films on Si (100) substrate are shown in Figure 1, which annealed at 600, 700, 800, 900℃ in flowing oxygen, respectively. It exhibits that all the main diffraction peaks belonging to ABO_3 phase are observed in the 2θ scanning range from 20° to 60°, implying that the $LaMnO_3$ film is single phase with pseudocubic structure, no other peaks appear, indicating that $LaMnO_3$ is a pure phase. Annealed at 600℃, only the Si (200) diffraction peak appears, along with an obvious $LaMnO_3$ amorphous cladding, the diffraction peaks of $LaMnO_3$ (110) and Si (200) coincide. Annealed at 700℃, the peaks of (111) and (211) appeared in XRD, and the peaks of (100) and (200) continued to increase when the annealed temperature increased to 800℃, however, the intensity of (111) and (211) diffraction peaks decreased to very small values, indicating that the LaMnO3 has a certain (h00) preferential orientation annealed at 800℃. The intensity of (100) and (200) peaks weaken while (111) and (211) peaks enhance at 900℃. From the above results, it can be seen that LaMnO3/Si films have the best (h00) preferred orientation annealed at 800℃.

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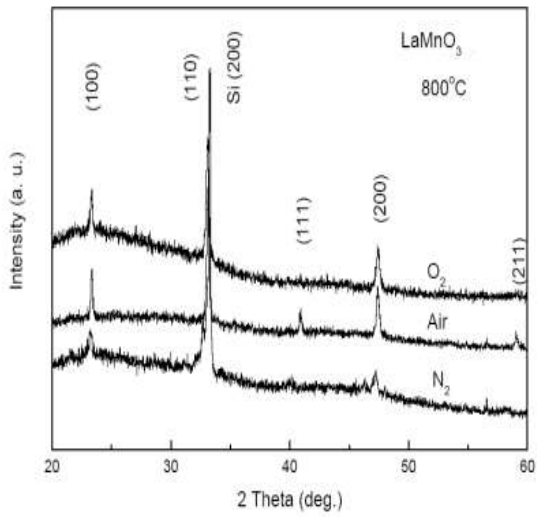

Figure 2 XRD diffraction pattern of LaMnO3/Si films are annealed at 800 ℃ in oxygen, air and nitrogen atmosphere.

The standard θ-2θ XRD patterns for the $LaMnO_3$ films on Si (100) substrate annealed at 800℃ in different atmospheres are shown in Figure 2. LaMnO3 film is obvious (h00) preferential orientation and weak (211) peak in O_2 atmosphere. In air, LaMnO3 film is obvious (h00) , (111) and (211) peak. In N_2, due to the lack of oxygen, the peak value of LaMnO3 is very weak, and the impurity peak appears. The results show that the preferred orientation (h00) of LaMnO3 is easily formed after annealing in oxygen-enriched atmosphere.

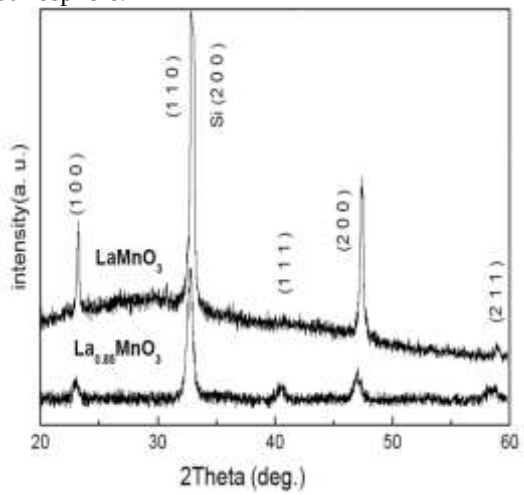

Figure 3 XRD patterns for $LaMnO_3$ and $La_{0.85}MnO_3$ films annealed at 800℃.

The XRD patterns for the $LaMnO_3$ and $La_{0.85}MnO_3$ films annealed at 800℃ are shown in Figure 3. LaMnO3 film is of (h00) orientation, and $La_{0.85}MnO_3$ film is of random orientation, (h00) orientation of $La_{0.85}MnO_3$ film is suppressed with La-deficient. It can be seen that the (200) peak of $La_{0.85}MnO_3$ films slightly shift to lower angle with the La-deficient, which reveals the increase of a-axis lattice parameter caused by La-deficient.

The temperature dependence of the resistance for the $LaMnO_3$ film is shown in Figure 4，under 0, 0.1 and 0.5 T applied field. It is found there exists an insulator-metal transition in the $LaMnO_3$ film, which can be attributed to the oxygen excess, produces mixed-valence Mn^{3+}-Mn^{4+} phases. The mixed valence activates the double-exchange interaction which promotes ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions giving rise to the MR effect. At zero fields, the temperature of insulator-metal transition, T_{MI}, obtained from the maximum resistance, is 190K. The temperature dependence of MR is plotted in the inset of Figure 4. Under 0.1 and 0.5 T applied field, it can be seen that the value of MR decrease with the increase of temperature. There is a significant MR effect only under a larger magnetic field of 0.5T, and the MR near T_{MI} is about 6% .

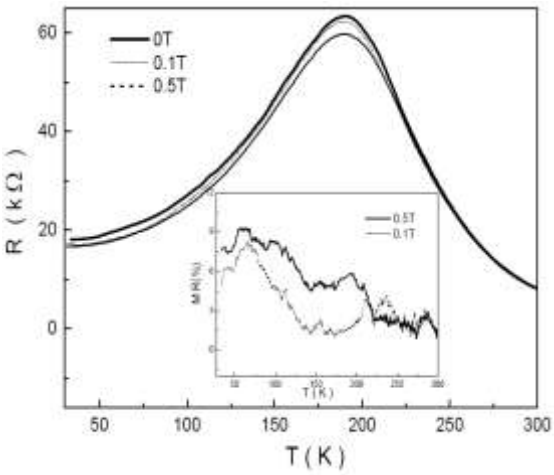

Figure 4 The temperature dependence of resistance for the LaMnO3 film.
The inset is the corresponding plot of MR versus temperature

The temperature dependence of the resistance for the $La_{0.85}MnO_3$ film is shown in Figure 5，under 0, 0.1 and 0.5 T applied field. At zero fields, the temperature of insulator-metal transition, T_{MI}, obtained from the maximum resistance, is 200K. The temperature dependence of MR is plotted in the inset of Figure 5. For the $La_{0.85}MnO_3$, under 0.1 T applied field, the value of MR decreases with the increase of temperature is 9.5% and 7.5% at 38, 180K, respectively, the MR shows a very slow drop with increasing temperature, and then the MR decreases above 180K, MR value as high as 2.7%

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at near to room temperature (270 K) is obtained, the films show an obvious low field magnetoresistance (LFMR), which is of importance for potential application[15] . This large LFMR is suggested to originate from the suppression of the spin-dependent scattering at the grain boundaries (GBs) [8].

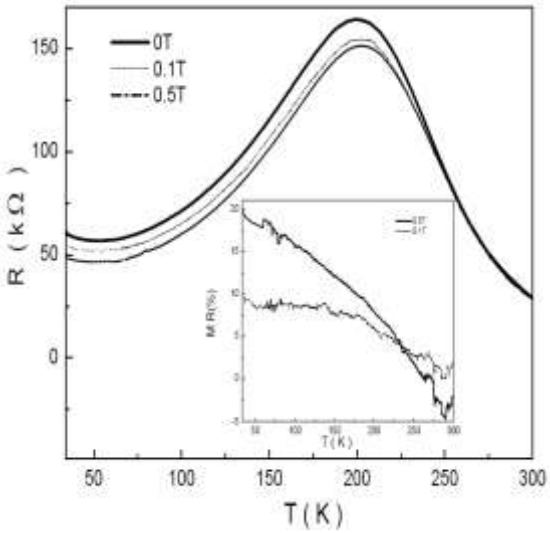

Figure 5 The temperature dependence of resistance for the La0.85MnO3 film.
The inset is the corresponding plot of MR versus temperature

IV. CONCLUSION

$LaMnO_3$ and $La_{0.85}MnO_3$ films were successfully prepared on Si substrates using a sol-gel method. The results show that temperature and atmosphere can obviously affect the orientation of $LaMnO_3$ films. The results of transport properties indicate that due to excessive oxygen, $LaMnO_3$ also undergoes a metal insulator transition; $La_{0.85}MnO_3$ has a large LFMR, which is of great significance for practical applications.

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