Structural and magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ferromagnetic thin film grown on PMN-PT by sol-gel method

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We report the preparation of epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films grown on (001)-oriented $0.72\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.28PbTiO_3 substrates by the sol-gel technique. The phase structure, magnetic properties and magnetoresistance of the samples are investigated by using high resolution X-ray diffraction, atomic force microscopy, physical property measurement system, respectively. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films display a well-defined hysteresis loop and typical ferromagnetism behavior at lower temperature. High magnetoresistance at 5 T of 42% appears at 227 K for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film.

Keywords: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films; PMN-PT; sol-gel method; magnetoresistance.

1. Introduction

The colossal magnetoresistance (CMR) effects in hole-doped manganite have attracted significant interest in the past decade due to their potential applications in magnetic random access memory, disk-driven read heads, magnetic field sensors and infrared detectors.^{1,2} In order to meet the severe requirements of the application, it is necessary to get the high quality thin films using cost-effective techniques with well-controlled properties. In recent years, magnetic $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ thin films grown on ferroelectric substrates have attracted more and more attention with great potential applications in CMR effects, especially on PMN-PT ferroelectric substrates.^{3–8} Thiele *et al.*³ successfully prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) epitaxial film on PMN-PT (001) ceramic substrates by pulse laser deposition (PLD) method and observed an obvious electric field modification of magnetization in this composite system. Zheng *et al.*⁶ obtained $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ /PMN-PT epitaxial thin film by magnetron sputtering and found that the resistivity of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films could be dynamically tuned by the electric field induced lattice strain via the converse piezoelectric effect in the PMN-PT.

However, there are few reports on the structural and magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ferromagnetic thin film grown on (001)-oriented PMN-PT single crystal by sol-gel method. In this study, we successfully prepared the epitaxial $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ferromagnetic film on PMN-PT by sol-gel method. The phase structure, magnetic properties and

magnetoresistance (MR) of the samples were investigated by using high resolution X-ray diffraction (XRD), atomic force microscopy (AFM), physical property measurement system (PPMS), respectively. Our results demonstrate that sol-gel method can provide an alternative approach for the preparation of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ epitaxial films on PMN-PT substrates.

2. Experimental

The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ precursor solution was prepared according to the stoichiometric formula $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. Appropriate amounts of lanthanum (III) nitrate hydrate $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, strontium acetate $\text{C}_4\text{H}_6\text{O}_4\text{Sr} \cdot 1/2\text{H}_2\text{O}$, manganese(II) chloride tetrahydrate $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were used as starting reagents, acetic acid glacial and deionized water were used as solvents. All chemicals used in this work were analytical reagent. The mixture solution was continuously stirring at 70°C for about 1 h to form transparent solution. And then the solution was filtered using a syringe and used as the precursor solution to deposit the LSMO thin film. The concentration of final solution was 0.4 mol/L in this case.

The PMN-PT substrate was pre-heated at 400°C for 30 min to release the stress and keep the surface clean. Then, the precursor solution was dropped and spin-coated on the PMN-PT substrates at 3000 rpm for 30 s. The wet films were baked at 400°C for 90 s and then annealed at 750°C for

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20 min in a rapid thermal processing furnace. The process of coating-heat treatment was repeated for six times to meet the demand thickness.

The crystalline phases and surface morphologies characterization of the films were examined by using X'Pert PRO high resolution XRD and Bruker atomic force microscopy (Ico, AFM), respectively. The resistivity and MR of the films were investigated by a four-point technique using physical property measurement system (PPMS, Quantum Design). The resistivity measurement was carried out in a temperature range 10–370 K without an externally applied magnetic field and with a 5 T magnetic field applied in the plane of the film, respectively. The MR at different temperatures was investigated accordingly.

3. Results and Discussion

Figure 1 shows the XRD θ - 2θ scan, rocking curve, and ϕ (ϕ) scans of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film on (001)-oriented PMN-

PT single crystal substrate by sol-gel methods. As can be seen from the θ - 2θ scan in Fig. 1(a), strong (001) peaks appear and no other peak characteristics of other phases can be found for the PMN-PT substrate. Only (001) and (002) peaks from pseudo-cubic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ can be observed, indicating that the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film is preferentially oriented along the C-axis perpendicular to the substrate surface. The inset of Fig. 1(a) is a rocking curve measured on the (002) peak of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films. The full width at half-maximum of the rocking curve is about 1.38° . The in-plane orientation between the film and the substrate is characterized by XRD ϕ -scans on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (022) and PMN-PT (022) peaks, as shown in Fig. 1(b). Based on Fig. 1, it is clear that the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film is epitaxially grown (cube-on-cube) on PMN-PT. The hetero-epitaxial relationship between the film and the substrate can be described as $(001)_{\text{LSMO}} \parallel (001)_{\text{PMN-PT}}$ and $[100]_{\text{LSMO}} \parallel [100]_{\text{PMN-PT}}$. Our experimental results demonstrate that sol-gel method can provide an alternative approach for the preparation of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ epitaxial films on PMN-PT substrates.

Figure 2 shows reciprocal space maps (RSMs) about (a) (001), (b) (013) and (c) (103) plane reflections of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PMN-PT}(001)$ thin film. For RSM⁷ chart of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-PMN-PT}(001)$, centers of both films and substrates are coincident on the Q_x , and their values are set as 0. The crystal cell parameters can be calculated through the symmetry plane. The parameter c of the PMN-PT and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film are $4.022 \text{ \AA}$ and $3.88 \text{ \AA}$, respectively. For RSM chart of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{-PMN-PT}(013)$ and (103), the center is not coincident on the Q_x shaft, indicating they are the asymmetrical plane. Through the asymmetrical plane inside, the crystal cell parameters can be detected and the parameters a , b can be calculated. The parameter b of the PMN-PT and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film are $4.022 \text{ \AA}$ and $3.91 \text{ \AA}$, respectively. The parameter a of the PMN-PT and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film are $4.022 \text{ \AA}$ and $3.89 \text{ \AA}$, respectively.

Figure 3 shows the atomic force microscopy 2 dimension image of the samples over an area of $1 \mu\text{m} \times 1 \mu\text{m}$ by tapping mode. The surface structures of the sample are compact and uniform. The grain size of the aggregations is measured and the average value is about 50 nm in diameter and $\pm 20 \text{ nm}$ in the height profile. The root mean square roughness (R_{rms}) of the films surface is calculated as 14.9 nm.

Figure 4 shows the typical magnetic hysteresis loop of the LSMO thin film at 300 K and 10 K, respectively. The LSMO thin films display a well-defined hysteresis loop and typical ferromagnetism behavior at lower temperature (10 K) than those measured at 300 K. The change of hysteresis loops with temperature of the samples is attributed to the paramagnetic-ferromagnetic phase transition. Moreover, the much higher saturated field value at lower temperature can be due to the much pinning centers at low temperature.^{9,10} The lower-right inset of Fig. 4 shows temperature dependence magnetic moment measurement from 10 K to 400 K of the sample with

Fig. 1. XRD patterns of a $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film on a PMN-PT substrate. (a) Normal θ - 2θ scan, the inset shows the rocking curve measured on the (002) peak of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$; (b) ϕ -scans on both the (022) of the substrate and the film.

Fig. 2. RSMs about (a) (001), (b) (013) and (c) (103) reflections of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film on PMN-PT.

Fig. 3. AFM images of the surface profile of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PMN-PT}$ film.

Fig. 4. Magnetic hysteresis loop of the LSMO thin film on PMN-PT measured at 300 K and 10 K, respectively. The lower-right inset shows temperature dependence magnetic moment measurement from 10 K to 400 K of the sample.

500 Oe magnetic field perpendicular to the sample applied. The moment decreases with the increase of temperature. The Curie temperature is measured and its value is about 370 K, which is similar to the bulk $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

The temperature dependence resistivity (ρ) curves of the samples without magnetic field (0 tesla) and with applied magnetic field of 5 tesla are shown in Fig. 5. The resistivity of the LSMO film without applied magnetic field increases with the increasing of temperature from 10 K and reaches the maximum value ($85 \Omega\text{-cm}$) around 290 K. With further increase of temperature, the resistivity begins to decrease accordingly. The resistivity of the film under 5 T magnetic fields shows the same trend with the increase of temperature. The maximum value of $60 \Omega\text{-cm}$ appears at 321 K. It can be seen that the peak of resistivity is depressed and the transition

Fig. 5. Resistivity versus Temperature data for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film without magnetic field (0 tesla) and with applied magnetic field of 5 tesla. The inset picture shows the magnetoresistance effect at 5 T as a function of temperature for the samples.

temperature increases with applied magnetic field. In order to investigate the MR effect of the LSMO thin films on PMN-PT substrate at different temperatures, the temperature dependent MR of the samples under an applied field of 5 T is measured and plotted in the inset of Fig. 5. MR values are calculated using the equation $\text{MR} = (\rho_H - \rho_0)/\rho_0 \times 100\%$, where ρ_0 and ρ_H are the resistivity values at zero and applied “H” magnetic field. From the curve, we can find that the maximum MR value under 5 T is about 42% at 227 K.

4. Conclusions

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films are prepared by the sol-gel method on (001)-oriented PMN-PT substrate. XRD results show that the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film is preferentially oriented along the C-axis perpendicular to the substrate surface and can epitaxially grow (cube-on-cube) on PMN-PT. The surface structures of the sample are compact and uniform. The grain size of the aggregations is measured and the average value is about 50 nm by using AFM techniques. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films display a well-defined hysteresis loop and typical ferromagnetism behavior at lower temperature. The T_c is about 370 K. High MR at 5 T of 42% appears at 227 K for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film.

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