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Preparation of Epitaxial $La_{0.7}Sr_{0.3}MnO_3$ Thin Films by Sol-gel Method

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ABSTRACT
The epitaxial $La_{0.7}Sr_{0.3}MnO_3$ thin films was prepared by sol-gel method on $LaAlO_3$ (100) single crystal. The orientation of the films at different annealing temperatures is studied: with the increase of temperature, the orientation of the films becomes better.

Keywords: Magnetoresistance; Thin film; Sol-gel

I. INTRODUCTION

Magnetoresistance effect is the phenomenon that the resistivity of materials changes under the action of external magnetic field. For Normal non-magnetic metals, such as Au and Cu, the effect is small. In 1954, Volger et al. measured the conductivity of Perovskite (structure) magnetic oxides and found that 10% magnetoresistance was observed in the $La_{0.7}Sr_{0.3}MnO_3$ system at 0.3T applied magnetic field. In 1993, Helmolt et al of the Siemens in Germany observed a larger magnetoresistance effect in $La_{2/3}Ba_{1/3}MnO_3$ films, which initiated the study of the magnetoresistance properties of Perovskite (structure)[1-3]. Recent studies show that the magnetic transition temperature and magnetic moment of Manganites vary with the doping composition, and the structure of manganites also changes greatly with the doping composition, i. e. from low symmetry to high symmetry. The magnetoresistance in doped oxide epitaxial films can reach 10^5-10^6%, and the maximum value of the magnetoresistance is near the M-I transition temperature and T_C, which is closely related to the structure change. Because of its large magnetoresistance, the magnetoresistance effect in this Perovskite (structure) is called Colossal magnetoresistance effect(CMR). Now, of course, the colossal magnetoresistance effect has lost its meaning, being used to distinguish it from the Giant magnetoresistance in magnetic metal multilayers, and must mean that its magnetoresistance is very large. At present, the colossal magnetoresistance effect of rare-earth Manganese Oxides has attracted the attention of many research groups worldwide due to its potential industrial applications, such as magnetic sensors and Disk read-write heads, has become one of the most active fields in the condensed matter physics[4-6].

It is well known that 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 and so on. These methods can produce high-quality films; However, its production area is limited and it needs to be operated in a vacuum chamber, so the cost is very high. Chemical vapor method can prepare large-area films, but its precursor colloids are difficult to prepare. Compared with the chemical vapor method, the sol-gel method is safer[8].

At present, one of the main problems in the application of colossal magnetoresistance materials is that the magnetoresistance near room temperature is too small in a small magnetic field, which is not enough for practical application. $La_{0.7}Sr_{0.3}MnO_3$ has a Curie temperature higher than room temperature, indicating that its MR effect can be used at room temperature.Therefore, many research groups focus on the low field magnetoresistance effect of $La_{0.7}Sr_{0.3}MnO_3$.

In this paper, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)films are successfully prepared by the sol-gel method on $LaAlO_3$ (LAO)(1 0 0) single crystal substrates. The epitaxy of the films is investigated at different annealed temperature.

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II. EXPERIMENTAL PROCEDURES

For preparation of $La_{0.7}Sr_{0.3}MnO_3$ thin films, $LaAlO_3$ (1 0 0) single crystals were chosen as substrates. The solutions of $La_{0.7}Sr_{0.3}MnO_3$ were synthesized from commercially available chemicals. In brief, stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(CH_3COO)_2 \cdot 0.5H_2O$ and $Mn(CH_3COO)_2 \cdot 6H_2O$ were dissolved gradually in a water/ethanol (v/v, 1:9) solution containing citric acid. The molar ratio of metal ions and citric acid was 1:2. Polyethylene glycol (PEG, molecular weight, 20,000) was used as surfactant to prevent the colloidal particles of chelate from aggregation. All chemicals used in this work were analytical reagents. The solution was diluted with water and ethanol to a 0.2–0.3 M solution in water/ethanol (v/v, 1:9). The solution was filtered (pore size in filter: 0.2 μm), and the substrates were ultrasonically cleaned using acetone, ethanol and water sequentially. Deposition of LSMO 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.

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

III. RESULTS AND DISCUSSION

In order to study the effect of heat treatment temperature on the orientation of $La_{0.7}Sr_{0.3}MnO_3/LaAlO_3$ film, LSMO film samples on LAO single crystal were annealed at 800 ℃ and 900 ℃, and the corresponding XRD diffraction pattern is shown in Figure 1. It can be seen from the figure that the film is perovskite pseudocubic structure. When annealed at 800℃, the diffraction pattern of the film contains not only (100), (200), (300) diffraction peaks, but also (110) and (211) diffraction peaks. Among them, (h00) is a strong peak, (110) and (211) are very weak peaks. The diffraction peak of the film is very close to the peak of the substrate LAO, because the lattice constant of the film and the substrate is very close, and the film grows along the (h00) direction of the substrate. However, there are other peaks, indicating that the growth is not complete (h00); When the annealing temperature rises to 900℃, only (h00) diffraction peaks of (100), (200) and (300) appear in the diffraction pattern, and there are no other heteropeaks, and the intensity of the peaks increases, indicating that with the increase of temperature, the orientation degree of the film increases, it grows in the complete (h00) direction and has good a-axis orientation.

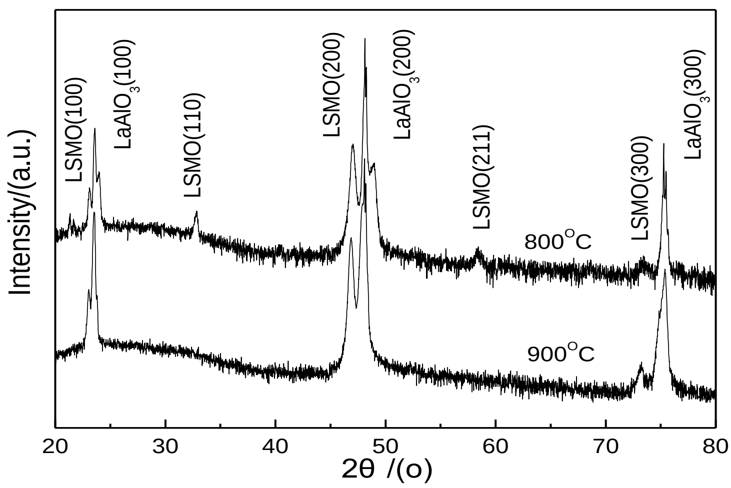

Figure 1 XRD diffraction patterns of LSMO /$LaAlO_3$ thin films at different annealing temperatures

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In order to further judge the epitaxy of the film, the rocking curve of (200) diffraction peak - out of plane orientation and phi scanning - in-plane orientation of (220) diffraction peak were measured.

Figure 2 is the rocking curve of (200) diffraction peak of LSMO film at different annealing temperatures, with a fixed value of 2θ = 46°。Figure 2 (a) The full width of half maximum (FWHM) of the diffraction peak in is 0.9°, but there are double peaks in the (200) diffraction peak, which may be due to the poor crystallization of LSMO; The FWHM in figure 2(b) is 1.0°. FWHM is an important index to measure the epitaxial properties of thin films. For the films prepared by chemical method, when FWHM is less than 1.0°, it can be considered to have better epitaxial growth. The results show that the films have good out of plane orientation.

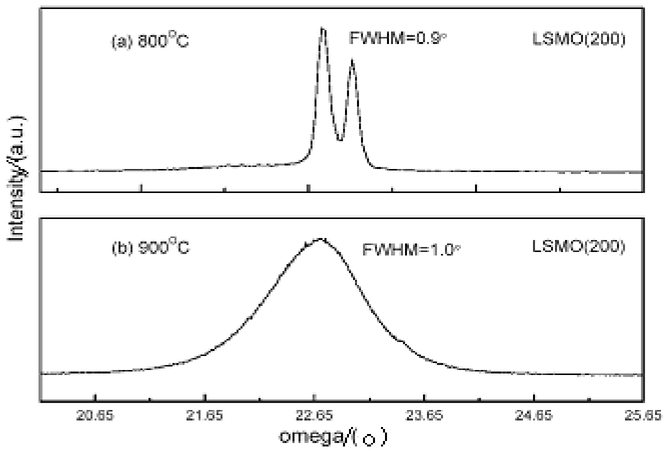

Figure 2 The rocking curve of LSMO film at different annealing temperatures

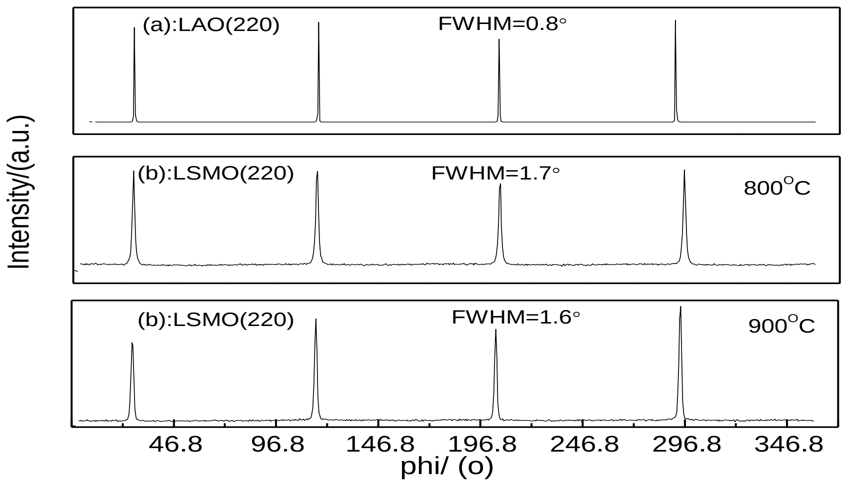

Figure 3 The phi scanning results of (220) diffraction peaks of LSMO film （a）LAO，（b）800℃，（c）900℃

Fig. 3 shows the phi scanning results of (220) diffraction peaks of LSMO film at different annealing temperatures. It can be seen that the film is of the four-fold symmetry and grown on the $LaAlO_3$ substrate in cube-on-cube mode. From the FWHM results of phi scanning, it can be seen that the film is 1.7^o at 800 ℃ and 1.6^o at 900℃. From 800 ℃ to 900 ℃, the in-plane orientation of LSMO/LAO films is improved with the increase of temperature. Compared with 0.8^o of $LaAlO_3$ single crystal, the LSMO/LAO film has better in-plane and out of plane orientation [11].

IV. 4. CONCLUSION

LSMO/LAO thin films were successfully prepared by sol-gel method. With the increase of annealing temperature, the orientation degree of the films increased. The samples annealed at 900 ℃ grew in the complete (h00) direction, had good a-axis orientation, and had better in-plane and out of plane orientation than those annealed at 800 ℃.

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