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Effect of Post Annealing on $La_{0.7}Sr_{0.3}MnO_3$ Thin Films

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The stability of $La_{0.7}Sr_{0.3}MnO_3$ thin films fabricated by pulsed laser deposition, under different annealing procedures, was investigated. $La_{0.7}Sr_{0.3}MnO_3$ films were deposited on (100) $LaAlO_3$ substrates at 650°C with the films thickness from 20 to 50 nm. The oxygen pressures used to fabricate the films were 150 mTorr and 100 mTorr. Then *in situ* annealing steps were performed at 100 and 150 mTorr, respectively. Curie temperatures (T_c) of the films were estimated from the peaks of the temperature dependent resistance data. For the films deposited at 100 mTorr and annealed at 150 mTorr, T_c slightly dropped for short annealing time and recovered to 360 K for 30 min annealing. For the films deposited at 100 mTorr and annealed at 150 mTorr, it maintained semiconducting behavior without transition after annealing up to 30 minutes. For *ex situ* post annealing, it was found that the T_c of the films strongly depended on the annealing procedures.

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1. Introduction

Doped perovskite manganites such as $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) are intensively studied as ferromagnetic materials for spintronic applications, due to their high Curie temperature ($T_c > 370$ K) and high spin polarization [1]. According to the theory based on double exchange interactions [2, 3], ferromagnetic and metallic properties of perovskite manganite are related to the interaction between pairs of Mn^{3+} and Mn^{4+} ions. Because interactions between pairs of Mn^{3+} and Mn^{4+} ions can be controlled by oxygen content, T_c of the film can be modified by controlling oxygen pressure during deposition [4].

In multilayer fabrication, different growth conditions may be used for each layer, with various annealing processes performed on the films, sometimes *ex situ*. Thus, the stability of the layers needs to be studied in order to obtain the desired multilayer structures. Dho and Hur [4] and Sun et al. [5] showed that oxygen deficient LSMO can have T_c increased by annealing at high oxygen pressure. Du et al. [6] reported that annealing at high temperatures can enhance ferromagnetic ordering and reduce coercivity. These works were concentrated mainly on oxygen deficient LSMO annealed *in situ* at high oxygen pressure and temperature. In this work, we have investigated the effect of post annealing, and focused on *in situ* and *ex situ* annealing with oxygen pressure different from deposition pressure. The results give useful guidelines for epitaxial multilayer deposition and annealing processes.

2. Experimental details

LSMO thin films were deposited on $LaAlO_3$ (LAO) (100) substrates at 650°C by pulsed laser deposition. A laser fluence of 3.6 J cm^{-2} and frequency of 5 Hz were used during deposition. The chamber base pressure during deposition and annealing processes was 5 mTorr. During the film deposition processes, oxygen was filled at 650°C and the substrate was annealed 10 min before ablation. The thickness of the films, ranging from 20 nm to 50 nm, was controlled by the deposition time (deposition rate 20 nm/min).

Table I and II summarize the annealing procedures employed during this study. For *in situ* post annealing study (Table I), the films were deposited at 150 mTorr (method 1) and 100 mTorr (method 2). Without switching off the heater, the deposited films were annealed at 100 mTorr and 150 mTorr, respectively, for different times. After annealing, the films were cooled down to room temperature naturally at the corresponding annealing pressure. For *ex situ* post annealing study (Table II), the films were deposited at 150 mTorr and cooled down to room temperature naturally at the same pressure. Then the films were heated up to 650°C with (method 4) and without (method 3) oxygen filled into the cham-

TABLE I

Annealing procedure for *in situ* post annealing processes. RT = room temperature.

Procedures	Temperature [°C]	Oxygen pressure [mTorr]	Duration [min]
Method 1			
pre annealing	650	150	10
deposition	650	150	2.5
post annealing	650	100	10,20,30
cooling	650 →RT	100	≈ 60
Method 2			
pre annealing	650	100	10
deposition	650	100	2.5
post annealing	650	150	0,5,20
cooling	650 →RT	150	≈ 60

TABLE II

Annealing procedure for *ex situ* post annealing processes. RT = room temperature.

Procedures	Temperature [°C]	Oxygen pressure [mTorr]	Duration [min]
Method 3			
pre annealing	650	150	10
deposition	650	150	2.5
cooling	650 →RT	150	≈ 60
heating	RT→ 650	no	≈ 30
annealing	650	150	10,30,60
cooling	650 →RT	150	≈ 60
Method 4			
pre annealing	650	150	10
deposition	650	150	2.5
cooling	650 →RT	150	≈ 60
heating	RT→ 650	150	≈ 30
annealing	650	150	10,30,60
cooling	650→RT	150	≈ 60

ber and annealed for different times. Finally, the films were cooled down to room temperature with the oxygen pressure maintained at 150 mTorr.

Resistance of the films was measured in the temperature range from 150 K to 380 K. Four rectangular shape gold electrodes were deposited on the films by sputtering through a mechanical mask. The peaks of resistance against temperature were used to estimate the Curie temperature of the films [7].

3. Results and discussions

3.1. In situ post annealing

Figure 1 shows the resistance against temperature of LSMO films grown on LAO at 150 mTorr and then annealed at 100 mTorr with different times. As the post annealing time increased from 0 min to 30 min, the Curie temperature increased from 330 K to 365 K. The film without annealing shown in Fig. 1 (curve *e*) has a higher resistance compared with the annealed film shown in Fig. 1 (curves *a*–*d*). One of possible reasons is that when oxygen pressure was changed to 100 mTorr, oxygen diffused out of the film. As a result, the ratio of Mn^{4+}/Mn^{3+} decreased and ferromagnetic ordering was reduced. However, other possibilities exist such as crystallinity change [5] and strain relaxation [4] which can affect the change of T_c. Dho and Hur [4] reported the results of X-ray diffraction (XRD) measurements, for T_c change from 300 K to 360 K. The change of out of plane lattice constant was 0.02 nm. We have performed XRD measurements on all the films, and the change in XRD profile was not significant due to the change of T_c which is about 30 K.

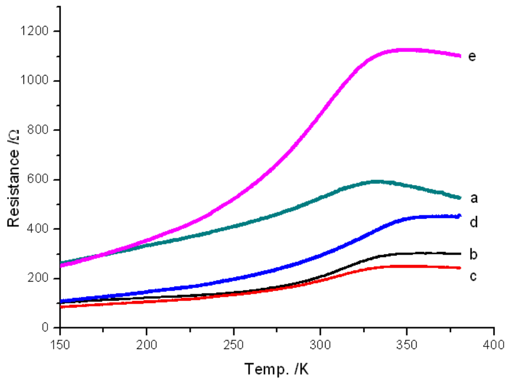

Fig. 1. Temperature dependent resistance curves of the films prepared by method 1 with different annealing times: (*a*) 0 min, (*b*) 10 min, (*c*) 20 min, (*d*) 30 min, (*e*) without post annealing (cooling under 100 mTorr after deposition).

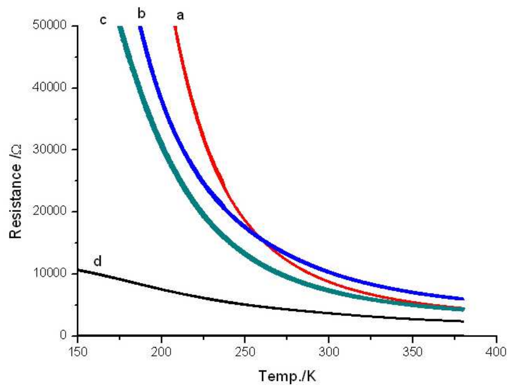

Fig. 2. Temperature dependent resistance curves of the films prepared by method 2 with different annealing times: (*a*) 0 min, (*b*) 5 min, (*c*) 20 min, (*d*) without post annealing (cooling under 150 mTorr after deposition).

Figure 2 shows the resistance against temperature of the films grown on LAO at 100 mTorr and annealed at 150 mTorr for different durations. All the films show a semiconducting behavior from 150 K to 380 K. During the annealing at high oxygen pressure, the ratio of Mn^{4+}/Mn^{3+} can be increased by oxygen absorption since the films were oxygen deficient.

3.2. Ex situ post annealing

Figure 3 shows the temperature dependent resistance of LSMO annealed at 150 mTorr for different times. The films were heated up from room temperature to 650°C without filling oxygen until the temperature reached 650°C. It shows that T_c of the films drop from 340 K to 275 K. Figure 4 shows the temperature dependent resistance curve of LSMO annealed at 150 mTorr. Oxygen was filled

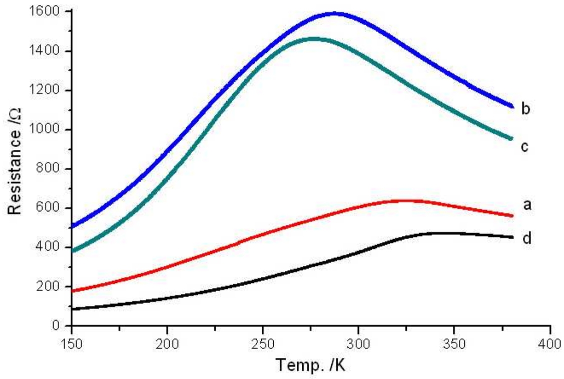

Fig. 3. Temperature dependent resistance curves of the films prepared by method 3 with different annealing times: (*a*) 10 min, (*b*) 30 min, (*c*) 60 min, (*d*) without post annealing (cooling under 150 mTorr after deposition).

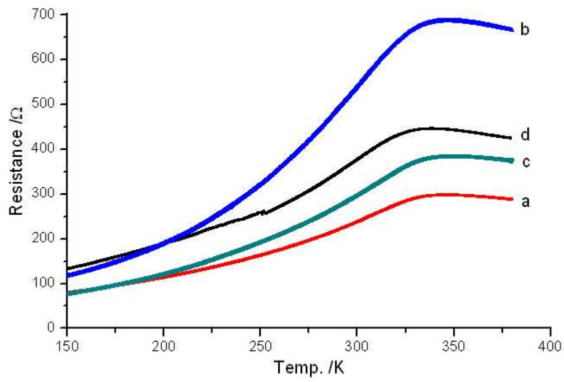

Fig. 4. Temperature dependent resistance curves of the films prepared by method 4 with different annealing times: (*a*) 10 min, (*b*) 30 min, (*c*) 60 min, (*d*) without post annealing (cooling under 150 mTorr after deposition).

when heating started at room temperature, and we observed that all the curves showed T_c about 340 K.

By comparing these two figures, we can observe that T_c of the films depends on the sequence of post annealing steps. When oxygen started to fill at 650°C, the films were under oxygen deficient condition during the heating stage. Thus, oxygen diffused out and caused T_c of the films to drop significantly. Great care has to be taken during the deposition and annealing processes, in order to ensure that the films preparation conditions are not altered by subsequent processing steps.

4. Conclusions

We have investigated the effect of post annealing of LSMO films under different annealing procedure. We found that stability of oxide film highly depend on oxygen environment, annealing steps and procedures. The work provides useful information for future studies of epitaxial oxide multilayer.

Acknowledgments

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