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Post annealing effect on transport properties of $La_{0.67}Ca_{0.33}MnO_3$ films grown on vicinal cut substrates

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ABSTRACT

$La_{0.67}Ca_{0.33}MnO_3$ thin films have been grown on 10°, 15°, and 20° vicinal cut $SrTiO_3$ (1 0 0) substrates by pulse laser deposition. The single phase and the least textured growth have been studied by X-ray diffraction analysis. The post annealing effect with high temperature and high oxygen pressure on the transport properties of films has been investigated by resistance versus temperature measurements. Films with post annealing show large enhancement of metal–insulator transition temperature T_p about 20–30 K towards higher temperature and obvious decrease of resistance, which is attributed to the refilling of oxygen, the change of Mn–O–Mn angle and the improvement of crystallinity by the post annealing effect. Specially, film on 20° vicinal cut substrate exhibits the biggest range gap of peak resistance drop, which may originate from more defects caused by steps at this tilt angle and many of these defects are removed after post annealing.

1. Introduction

The colossal magnetoresistive (CMR) manganese oxide $La_{1-x}Ca_xMnO_3$ has been studied intensively over several decades because of its potential applications in devices such as magnetic sensor, magnetoresistive read heads, and magnetoresistive random access memory (MRAM) [1–3]. Apart from these technological applications, $La_{1-x}Ca_xMnO_3$ thin films present other interesting properties. In particular, both the metal–insulator transition temperature (T_p) and the paramagnetic–ferromagnetic transition temperature (T_c) in $La_{1-x}Ca_xMnO_3$ films can be affected by many parameters, such as film thickness [4], strain [5–7], magnetic fields [8] and post annealing effect [7,9,10]. Moreover, $La_{1-x}Ca_xMnO_3$ films deposited on vicinal cut substrates by artificial tailor have attracted much attention [11–16]. This is because the film growth mechanism and the strain state of film grown on vicinal cut substrate have some difference with film on planar substrate and some unusual properties will appear [17]. $La_{1-x}Ca_xMnO_3$ films grown on vicinal cut substrates have been used to investigate the transport properties along different orientations [11] and the potential applications of photoelectric or thermoelectric devices based on the anisotropic thermoelectric properties [12–16]. However, the post annealing effect on transport properties of $La_{1-x}Ca_xMnO_3$ films grown on vicinal cut substrates has rarely been reported.

In this paper, we report the fabrication of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films grown on vicinal cut $SrTiO_3$ (STO) (1 0 0) substrates by pulse laser deposition (PLD) and the post annealing effect with high temperature and high oxygen pressure on the transport properties of these films. We show that the post annealing effect can obviously reduce the resistance, shift the transition temperature T_p towards higher temperature. Especially film on 20° vicinal cut substrates has some novel transport properties after post annealing.

2. Experimental

$La_{0.67}Ca_{0.33}MnO_3$ polycrystalline targets were sintered by the conventional solid state reaction method. $La_{0.67}Ca_{0.33}MnO_3$ films with thickness of 200 nm were deposited on 10°, 15°, 20° vicinal cut STO (1 0 0) substrates by PLD. The PLD process was performed by using a KrF excimer-laser of 248 nm in wavelength (λ) and 28 ns in pulse duration. An optimized laser fluency of 1.8 J/cm^2 and a repeat frequency of 5 Hz were utilized. For all of these films, the temperature of substrates and the pressure of oxygen were precisely kept, respectively, at 780 °C and 40 Pa during the deposition. Then these films were *in situ* annealing at 780 °C and oxygen pressure of 3000 Pa for 1 h. Detailed information concerning substrate preparation and film growth can be found in the literatures [18,19].

The phase structure and orientation of film was characterized by X-ray diffraction (XRD, Brucker Discover D8) machine with Cu Kα_1 radiation. The transport properties were studied by resistance versus temperature measurements using the four-probe method in the range from 77 K to 320 K. After this, these films underwent post annealing effect at 900 °C and oxygen pressure of 30,000 Pa for 0.5 h. Finally, the resistance versus temperature measurements were made again.

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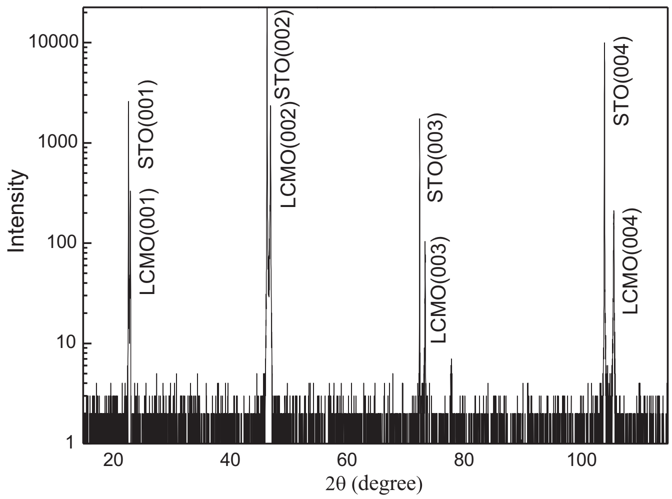

Fig. 1. XRD pattern of as-grown LCMO film on 10° vicinal cut STO (1 0 0).

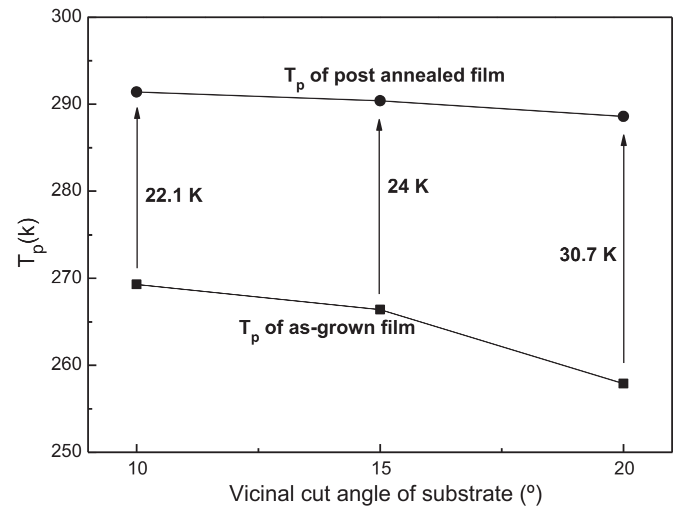

Fig. 3. Transition temperature T_p of as-grown films and post annealed films dependence of vicinal cut angles of substrates.

3. Results and discussion

In Fig. 1, the XRD pattern of a 200 nm thickness as-grown LCMO thin film grown on 10° vicinal cut STO (1 0 0) substrate is given. This pattern shows that, besides the peaks of substrate, only the LCMO film (0 0 l) reflections are presented. This indicates the phase purity and the least textured growth (along *c*-axis of substrate) of the film. Similar growth behaviors have also been found in LCMO thin films grown on 15° and 20° vicinal cut substrates.

The post annealing effect with high temperature and high oxygen pressure on the electric transport properties has been analyzed by the resistance versus temperature measurements in the range from 77 K to 320 K shown in Fig. 2. All of these films (including as-grown films and post annealed films) have high transition temperature T_p because of our preparation technology. Obviously, the as-grown films have greater resistance and lower transition temperature T_p compared with films underwent post annealing effect. As the tilt angle increases, the as-grown films display slightly decrease of transition temperature T_p and largely increase of resistance. This can be explained that there are more defects which heighten the resistance when the tilt angle increases. But after post annealing with high temperature and high oxygen pressure, the electric transport properties have some distinct changes. The resistance and its derivation to temperature (dR/dT) both dramatically become smaller, which is in agreement with other reports [7,9,10]. Fig. 3 shows the transition temperature T_p of as-grown films and post annealed films grown on vicinal cut substrates with different tilt angles and we can see that the transition temperature T_p is shifted towards higher temperature remarkably after post annealing, particularly the film on 10° vicinal cut substrate has a transition temperature T_p up to 291.4 K. The enhancement of transition temperature T_p by post annealing is larger than other reports [7,9,10,20], as 30.7 K (20° vicinal cut), 24 K (15° vicinal cut), and 22.1 K (10° vicinal cut). Both the decrease of resistance and the shift of transition temperature T_p cannot be explained in terms of a unique underlying mechanism. Many processes interplay together and should all be taken into account. Post anneal effect enables oxygen refill in the lattice again and reduces the oxygen deficit, resulting in the enrichment of Mn^{4+}/Mn^{3+} ratio and enhancement of double exchange [9,21,22]. Simultaneously, the crystallinity will be optimized and the inhomogeneity will be removed. Another important reason is that the relaxation of epitaxial strain caused by post annealing can make the Mn–O–Mn angle change, consequently the charge carries move easily between adjacent $Mn^{3+/4+}$ and the transition temperature T_p increases [20]. Additionally, films with post annealing have a broadening peak resistance at the metal–insulator transition region, which is the result of the phase coexistence and competition between insulating and metallic phases [4].

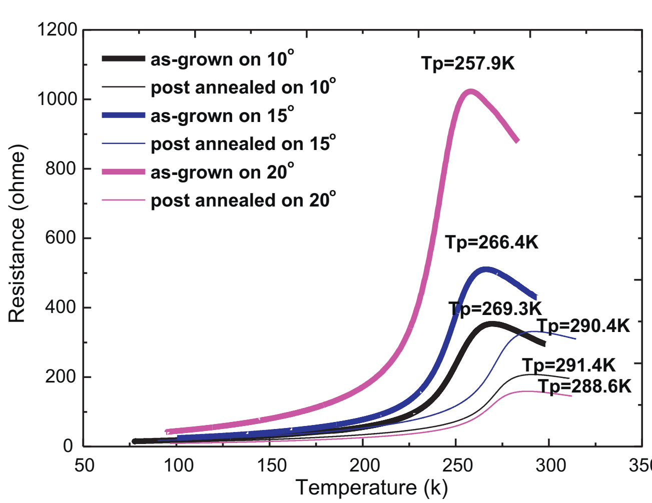

Fig. 2. Resistance versus temperature curves of films on 10°, 15°, and 20° vicinal cut STO (1 0 0).

An interesting phenomenon to be pointed out is that the resistance of film on 20° vicinal cut STO exhibits the biggest range gap of drop with post annealing effect. Fig. 4 shows the peak resistance of as-grown film (R_a), the peak resistance of post annealed film (R_p), as well as their ratio (R_a/R_p) dependence of vicinal degree of substrate. It can be seen from Fig. 4 that the ratio R_a/R_p of film on 20° vicinal cut STO is about 6.5, larger than other two. We can conclude that there are much more defects caused by steps at 20° tilt angle and most of these defects can be removed by post annealing with high temperature and high oxygen pressure.

4. Conclusions

The high temperature and high oxygen pressure post annealing effect on the transport properties of $La_{0.67}Ca_{0.33}MnO_3$ thin films on vicinal cut substrates has been studied. This effect can decrease the resistance greatly and make the metal–insulator transition temperature T_p shift towards higher temperature about 20–30 K, as

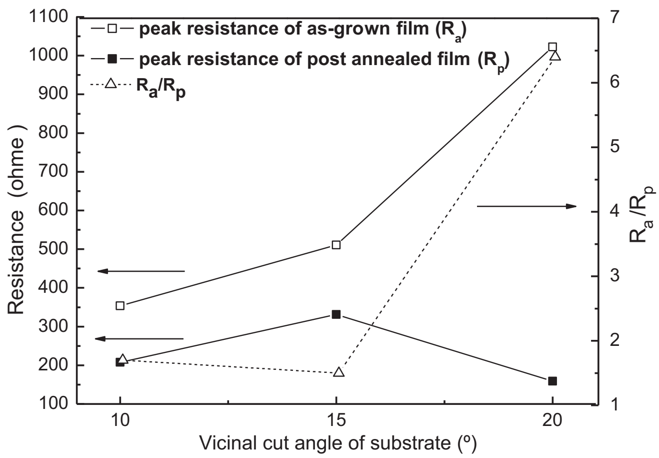

Fig. 4. Peak resistance of as-grown film, post annealed film and their ratio dependence of vicinal cut angles of substrates.

the oxygen content, Mn–O–Mn angle, Mn^{4+}/Mn^{3+} ratio and the crystallinity have changed. Especially, the film on 20° vicinal cut substrate has the largest drop of peak resistance, which can be explained that more defects caused by steps at this tilt angle can be removed by post annealing effect.

Acknowledgements

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