

## Large Magnetoresistance in La-Ca-Mn-O Films

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**Abstract** — A very large magnetoresistance value in excess of  $10^6\%$  has been obtained at 110K,  $H = 6T$  in La-Ca-Mn-O thin films epitaxially grown on  $\text{LaAlO}_3$  substrates by pulsed laser deposition. The as-deposited film exhibits a substantial magnetoresistance value of 39,000%, which is further improved by heat treatment. A strong dependence of the magnetoresistance on film thickness was observed, with the value reduced by orders of magnitude when the film is made thicker than  $\sim 2000 \text{ \AA}$ . This behavior is interpreted in terms of lattice strain in the La-Ca-Mn-O films.

### I. INTRODUCTION

Perovskite-like oxide of lanthanum manganite ( $\text{LaMnO}_3$ ) can be made to exhibit both strong ferromagnetism and metallic conductivity when La ions (3+ valence) are partially substituted with 2+ valence ions such as Ca, Ba, Sr, Pb and Cd. The substitution creates a  $\text{Mn}^{3+} - \text{Mn}^{4+}$  mixed valence state, creating mobile charge carriers and canting of Mn spins [1]-[6].

Thin films of the manganites have previously been prepared and their magnetoresistance (MR) reported for La-Ba-Mn-O [7] and La-Ca-Mn-O [8], with relatively small, negative MR ratios of about 100 - 200%. The MR ratio is defined here as  $\Delta R/R_H = (R_H - R_0)/R_H$  where  $R_0$  is the zero-field electrical resistance and  $R_H$  is the resistance in the applied field, typically near  $H = 6T$ . More recently, very large MR ratios have been reported in epitaxially-grown  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$  films on  $\text{LaAlO}_3$  substrates, with the MR value exceeding 100,000% [9], [10]. Large MR ratios in excess of 10,000% have been made possible in bulk, polycrystalline material as well by Y-doping [11].

In this paper, we report the magnetoresistance behavior of La-Ca-Mn-O films with a very large MR ratio of

$\sim 10^6\%$ . The temperature, field, and thickness dependences of magnetoresistance ratio are discussed.

### II. EXPERIMENTAL PROCEDURE

Thin films of La-Ca-Mn-O, 100-5000  $\text{ \AA}$  thick, were deposited on (100)  $\text{LaAlO}_3$  substrates by pulsed laser deposition. The substrate temperature was  $\sim 700^\circ\text{C}$ , and the oxygen partial pressure in the chamber was maintained at  $\sim 100 \text{ mTorr}$ . The dense target, with a nominal composition of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ , was prepared by the mixing of high-purity component oxides or carbonates and repeated grinding and sintering at  $\sim 1400^\circ\text{C}$  in an oxygen atmosphere.

The electrical resistance and magnetoresistance of the samples were measured as a function of temperature and magnetic field by four-point technique in a superconducting magnet. A constant current in the range of 5 nA-100  $\mu\text{A}$  was used. The R value and the MR ratio were found to be essentially independent of the current used. The maximum applied field was 6T, with the in-plane field direction parallel to the current direction. The MR ratio was always negative and isotropic.

### III. RESULTS AND DISCUSSION

The as-deposited La-Ca-Mn-O film,  $\sim 1000 \text{ \AA}$  thick, exhibited a MR ratio of 39,000% (at 100K,  $H = 6T$ ) which is substantially higher than the values of  $\sim 500\%$  that we reported previously [9], [10]. Subsequent heat treatment at  $850^\circ\text{C}/1\text{h}$  in a 3 atmosphere oxygen atmosphere dramatically improves the MR ratio to  $1.1 \times 10^6\%$  (at 110K,  $H = 6T$ ) which is the highest value ever reported for the La-Ca-Mn-O system. Shown in Fig. 1 is the resistivity vs field curve for the La-Ca-Mn-O film at 110K. The figure shows that the major part of the resistivity drop occurs at  $H < 2T$ . The zero field resistivity of  $\rho = 50.8 \Omega \cdot \text{cm}$  (resistance  $R = 4.13 \text{ M}\Omega$ ) is reduced to  $\rho = 4.61 \text{ m}\Omega \cdot \text{cm}$  ( $R = 375 \Omega$ ) when the in-plane applied field (parallel to the direction of the applied current) is increased to 6T. The

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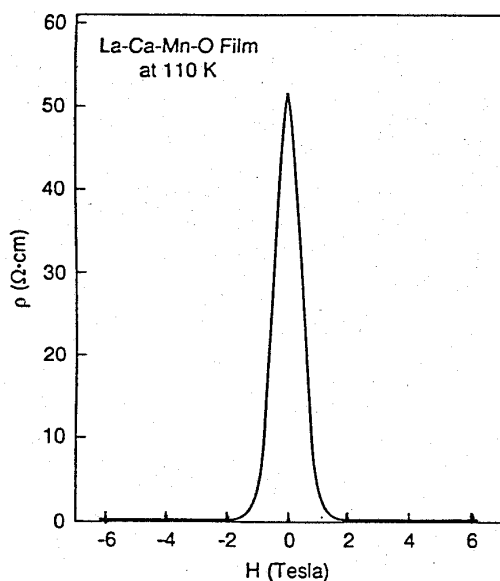


Fig. 1 Resistivity vs field curve for the La-Ca-Mn-O film at 110K.

exact reason why these samples, both the as-deposited and the heat treated films, exhibit higher MR ratios than our previous samples [9], [10] is not clearly understood at the moment. The general trend that we observed, however, is that denser targets (e.g., sintered at higher temperatures and longer times) produce better quality films with higher MR values.

Shown in Fig. 2 is the temperature dependence of  $\Delta R/R_H$  (at  $H = 6T$ ) of the heat treated La-Ca-Mn-O film of Fig. 1. The high MR values of  $10^4 - 10^6\%$  occur within a temperature range of about 100-150K. The MR becomes orders of magnitude smaller at temperatures outside this range by about 50K or more. The MR ratio is only 14% at 280K and 270% at 60K. The strong dependence of MR on temperature and the presence of a cusp in the  $\Delta R/R_H$  vs  $T$  curve observed in this film may be related to either semiconductor-to-metal or magnetic transition as discussed in previous publications [9], [10]. Further study is required to understand the exact mechanisms responsible for the observed MR behavior in La-Ca-Mn-O.

Another interesting phenomenon observed in the La-Ca-Mn-O films is the severe thickness-dependence of magnetoresistance, as shown in Fig. 3. The curve in Fig. 3 was obtained by using the highest MR data (at 110-230K,  $H = 6T$ ) for each film thickness after heat treatments under various conditions (750-950C for 1-12h) in an oxygen atmosphere. The curve shows a maxima at a film thickness of  $\sim 1000$  Å, with the highest MR ratio of 1.1 million %. The MR ratios for the films on either side of the peak in Fig. 3 are drastically lower. The values for the thicker films are  $\sim 1700\%$  for 2000 Å and  $\sim 1400\%$  for the 5000 Å thickness. The films substantially thinner than  $\sim 1000$  Å

also exhibit decreased MR ratios, e.g.,  $\sim 21,000\%$  for 500 Å thickness and 2200% for 100 Å thickness.

The observed thickness dependence of MR is tentatively attributed to the change in the lattice strain induced by the change in film thickness. In our recent report on the MR behavior of  $La_{0.67}Ca_{0.33}MnO_x$  thin films [9], [10], it was pointed out that the very large MR values ( $>100,000\%$ ) were obtainable, not in a polycrystalline form, but in an epitaxially grown films on single crystalline  $LaAlO_3$  with a lattice parameter of a  $\sim 3.791$  Å, smaller than that of the La-Ca-Mn-O material ( $a \sim 3.867$  Å). When deposited on polycrystalline yttria-stabilized zirconia substrate, or lattice-mismatched single crystalline substrates such as Si or MgO, the MR ratio of the film was very low. Thus it is quite possible that the very large magnetoresistance observed is directly related to the straining of the lattice, i.e., compressively by the epitaxy.

As the La-Ca-Mn-O film becomes thicker, the degree of epitaxial straining of its lattice by the  $LaAlO_3$  substrate decreases. The thicker films would then consist of strained, high-resistivity, high-MR region near the substrate and less strained low-resistivity, low-MR region away from the substrate. The low-resistivity region dominates the MR measurement as the applied current preferentially flows through it thus making the high-resistivity, high-MR region to become undetectable. The data in Fig. 3 and the aforementioned argument further support our hypothesis that the MR behavior in the La-manganites is closely related to the

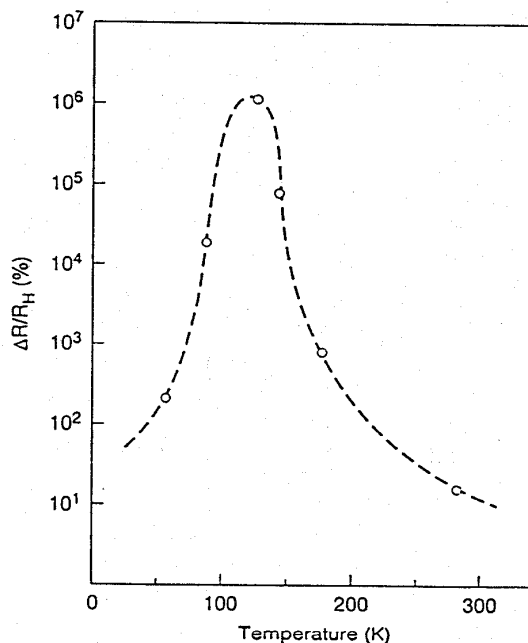


Fig. 2 Magnetoresistance ratio vs temperature curve for the La-Ca-Mn-O film.

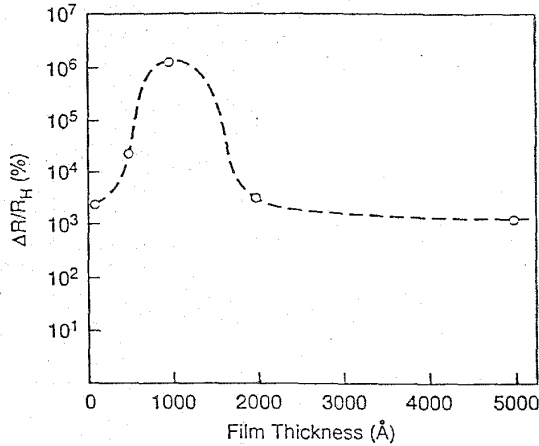


Fig. 3 Thickness dependence of  $\Delta R/R_H$  for the La-Ca-Mn-O film.

optimization of the perovskite lattice parameter, which would not be surprising in that the change in lattice parameter would affect the interatomic distance and bond angle, thus influencing the magnetic exchange interactions between two magnetic cations separated by an anion. It is also noteworthy that among the three well-known ferromagnetic perovskite manganites with the same stoichiometry (with La partially substituted with the Group IIA elements),  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ ,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_x$ , and  $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_x$ , only the La-Ca-Mn-O system exhibits the very large MR ratio of  $10^5 - 10^6\%$ . The La-Sr-Mn-O and La-Ba-Mn-O systems, either in the bulk form or in the similarly processed film form, exhibit very low MR ratios, typically less than  $\sim 500\%$ . The ionic radii of Sr and Ba (1.27 and 1.43 Å, respectively) are much larger than that of Ca (1.06 Å), and therefore the lattice parameters in the perovskite structure are correspondingly larger.

The reason why the La-Ca-Mn-O films much thinner than 1000 Å exhibit reduced MR ratios even though they are more strained by epitaxy is not yet known at the moment. It may be that there is an optimal lattice strain for the high MR phenomenon or there are some structural or chemical (e.g. oxygen stoichiometry) differences in these thinner films that influence the MR behavior. These thinner films also have high electrical resistance, e.g., the 500 Å thick film ( $2 \times 3$  mm size) exhibits  $R \sim 10$  MΩ and the 100 Å thick film,  $R \sim 18$  MΩ, and thus causing measurement difficulties and complications. Further work is needed to clearly understand these results.

The effect of lattice parameter on the MR behavior in La-Ca-Mn-O is also seen in polycrystalline (bulk) materials where the epitaxy is not involved. When bulk  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$  is modified by partial substitution of La

with Y into  $\text{La}_{0.60}\text{Y}_{0.07}\text{Ca}_{0.33}\text{O}_x$ , the lattice parameter is reduced from  $a \sim 3.867$  Å to  $a \sim 3.859$  Å [11]. The resultant change in MR behavior is dramatic in that the MR ratio in the Y-doped bulk material, without any epitaxial growth involved, can now be as high as 10,000% (at 140K,  $H = 6$ T) as compared to at most  $\sim 1000\%$  in the undoped La-Ca-Mn-O material. This result in bulk material can be viewed as consistent with the thickness dependence behavior in thin films in that the straining of lattice may play an important role in determining the MR behavior in the La-Ca-Mn-O system.

#### IV. SUMMARY

Magnetoresistance behavior in epitaxially grown La-Ca-Mn-O thin films has been investigated. Very large MR ratios as high as  $1.1 \times 10^6\%$  have been obtained. A strong dependence of the MR ratio on film thickness has been observed, which is attributed to the variation in lattice parameter caused by epitaxial straining of the La-Ca-Mn-O films.

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