Thickness dependence of magnetoresistance in La–Ca–Mn–O epitaxial films

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Colossal magnetoresistance in excess of 10^6% has been obtained (at 110 K, H=6 T) in epitaxially grown La–Ca–Mn–O thin films. The as-deposited film exhibits a substantial magnetoresistance value of 39 000%, which is further improved by heat treatment. The magnetoresistance is found to be strongly dependent on film thickness, with the value reaching the maxima at ~1000 Å thickness, and then reduced by orders of magnitude when the film is made thicker than ~2000 Å. This behavior is interpreted in terms of lattice strain in the La–Ca–Mn–O films. © *1995 American Institute of Physics.*

Lanthanum manganite ($LaMnO_3$) 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. A Mn^{3+}-Mn^{4+} mixed valence state produced by the substitution creates mobile charge carriers and canting of Mn spins.[1–6]

The magnetoresistance (MR) behavior of thin films of the manganites such as La–Ba–Mn–O and La–Ca–Mn–O, with relatively small, negative MR ratios of about 100%–200%, has been reported in recent years.[7,8] 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=6 T. More recently, very large MR ratios have been reported in epitaxially grown $La_{0.67}Ca_{0.33}MnO_x$ films on $LaAlO_3$ 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 letter, we report the MR behavior of epitaxial La–Ca–Mn–O films with a very large MR ratio of ~10^6%. The temperature, field, and thickness dependences of magnetoresitance ratio are discussed.

La–Ca–Mn–O, films, 100–5000 Å thick, were deposited on (100) $LaAlO_3$ substrates by pulsed laser deposition. Dense targets, with a nominal composition of $La_{0.67}Ca_{0.33}MnO_x$, prepared by mixing high-purity component oxides or carbonates and repeatedly grinding and sintering at ~1400 °C in an oxygen atmosphere, were used. The substrate temperature was ~700 °C, and the oxygen partial pressure in the chamber was maintained at ~100 mTorr.

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 μA was used. The R values and the MR ratios were found to be essentially independent of the current used. The maximum applied field was 6 T, with the in-plane field direction parallel to the current direction. The MR ratios were also negative and isotropic.

The La–Ca–Mn–O film (~1000 Å thick) in the as-doped condition exhibited a MR ratio of 39 000% (at 100 K, H=6 T) which is substantially higher than the values of ~500% that we reported previously.[9,10] Subsequent heat treatment at 850 °C/1 h in a 3 atm oxygen atmosphere dramatically improves the MR ratio to 1.1×10^6% (at 110 K, H=6 T) which is the highest value ever reported for the La–Ca–Mn–O system. [If expressed in $\Delta R/R_0$ (instead of $\Delta R/R_H$), the MR ratios are 99.744% and 99.991% for the as-deposited and the 850 °C/1 h heat treated films, respectively].

The temperature dependence of $\Delta R/R_H$ (at H=6 T) of the heat treated La–Ca–Mn–O film is shown in Fig. 1. The high MR values of 10^4–10^6% occur within a temperature range of about 100–150 K. The MR becomes orders of magnitude smaller when the temperature is ~40 K or more outside this range. For instance, the MR ratio is only 14% at 280 K and 270% at 60 K. The strong dependence of MR on temperature and the presence of a cusp in the $\Delta R/R_H$ versus T curve observed in this film are similar to that reported in our previous publications,[9,10] and may be related to either semiconductor-to-metal and/or magnetic transition. Further study is required to understand the exact mechanisms responsible for the observed MR behavior in La–Ca–Mn–O.

Shown in Fig. 2 is the resistivity versus field curve for the heat treated La–Ca–Mn–O film at 110 K. The figure shows that the major part of the resistivity drop occurs at H<2 T. The zero-field resistivity of ρ=50.8 Ω cm (resistance R=4.13 MΩ) is reduced to ρ=4.61 mΩ cm (R=375 Ω) when the in-plane applied field (parallel to the direction of the applied current) is increased to 6 T. The exact reason why

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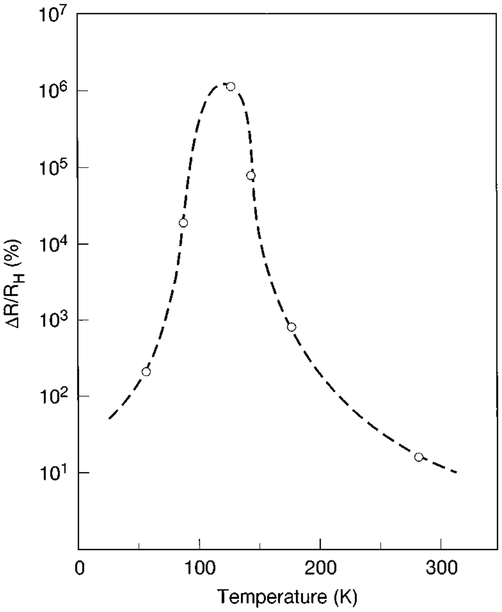

FIG. 1. Magnetoresistance ratio vs temperature curve for the La–Ca–Mn–O film.

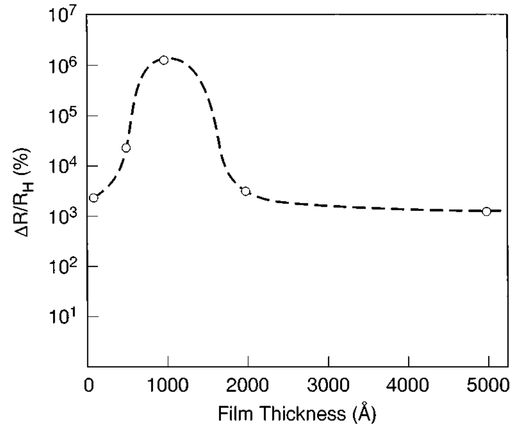

FIG. 3. Thickness dependence of $\Delta R/R_H$ for the La–Ca–Mn–O film.

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 and more uniform targets (e.g., sintered at higher temperatures and longer times) produce better quality films with improved epitaxy, less particulate incorporation, better chemical homogeneity and thickness uniformity, thus exhibiting higher MR values.

Interestingly, the magnetoresistance in the La–Ca–Mn–O films exhibits a strong dependence on film thickness as shown in Fig. 3. The curve in Fig. 3 was constructed by using the highest attainable MR value (at 110–230 K, H=6 T) for each film thickness after heat treatments under various conditions (750–950 °C for 1–12 h) in an oxygen atmosphere (3 atm). The curve shows a maximum at a film thickness of ~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 ~1700% for 2000 Å and ~1400% for the 5000 Å thickness. The films substantially thinner than ~1000 Å also exhibit decreased MR ratios, e.g., ~21 000% for 500 Å thickness and 2200% for 100 Å thickness.

It is hypothesized that the observed thickness dependence of MR is related 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 only in epitaxially grown films on single crystalline $LaAlO_3$ with a lattice parameter of ~3.791 Å, smaller than that of the bulk La–Ca–Mn–O material (a ~3.867 Å). When deposited on polycrystalline yttria-stabilized zirconia substrates or lattice-mismatched single crystalline substrates such as Si or MgO, the MR ratio of the film was very low, typically below ~500%. 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 imposed by the substrate with the smaller lattice parameter.

The degree of epitaxial straining of the La–Ca–Mn–O film lattice by the $LaAlO_3$ substrate is expected to decrease as the film becomes thicker. 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 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 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 or electronic 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 stoichi-

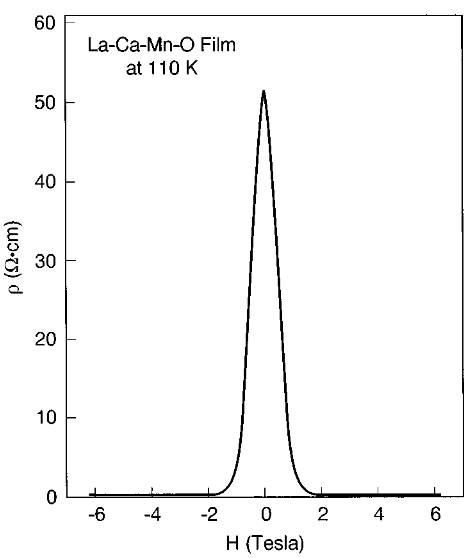

FIG. 2. Resistivity vs field curve for the La–Ca–Mn–O film at 110 K.

ometry (with La partially substituted with the Group IIA elements), $La_{0.67}Ca_{0.33}MnO_x$, $La_{0.67}Sr_{0.33}MnO_x$, and $La_{0.67}Ba_{0.33}MnO_x$, 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 ~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.

It would be interesting to systematically vary the lattice parameter of the La–Ca–Mn–O single crystal film and compare the MR behavior of the various samples with the same chemistry but with different lattice parameters. We are planning to carry out experiments to mechanically (elastically) deform the single crystalline films or bulk materials so as to quantitatively assess the effect of strain on resistivity and magnetoresistance properties. For example, the samples in Fig. 3 can be subjected to either lateral compression or bending (tensile or compressive) within the limit of substrate fracture stress so as to either increase or decrease the lattice parameter of La–Ca–Mn–O. If our hypothesis of the lattice strain effect is correct, we should see significant changes in R and MR behavior upon straining of the La–Ca–Mn–O material. The results of these experiments will be reported in future publications.

The reason why the La–Ca–Mn–O films much thinner than 1000 Å exhibit reduced MR ratios (Fig. 3), 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 (2×3 mm size) exhibits $R\sim10$ MΩ and the 100 Å thick film, $R\sim18$ MΩ, and thus causing measurement difficulties and complications. Diffusion-induced contamination from the substrate or diffusion-induced change in cation stoichiometry in the film is another possibility to be considered. Further work is needed to clearly understand these results.

We have observed the effect of lattice parameter on the MR behavior in La–Ca–Mn–O in polycrystalline (bulk) materials as well where epitaxy is not involved. When bulk $La_{0.67}Ca_{0.33}MnO_x$ is modified by partial substitution of La with Y into $La_{0.60}Y_{0.07}Ca_{0.33}O_x$, the lattice parameter is reduced[11] from a ~3.867 Å to $a\sim3.859$ Å. 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 140 K, $H=6$ T) as compared to at most ~1000% in the undoped material. This result in the 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.

In summary, we have investigated the magnetoresistance behavior in epitaxially grown La–Ca–Mn–O thin films. A colossal MR ratio as high as 1.1×10^6% has been obtained. A strong dependence of the MR ratio on film thickness has been observed, which is tentatively attributed to the variation in lattice parameter caused by epitaxial straining of the La–Ca–Mn–O films.

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