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Improved properties of $La_{2/3}Ca_{1/3}MnO_3$ thin films by addition of silver

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Thin films of Ag-added $La_{2/3}Ca_{1/3}MnO_3$ exhibit enhancement of several desirable characteristics over the pristine counterparts. We find that the addition of Ag results in a pronounced increase in the insulator–metal transition temperature (T_p) and ferromagnetic transition temperature (T_c). There is also a remarkable improvement in the magnetic and electrical homogeneity of the samples as indicated by narrower ferromagnetic resonance linewidths and narrower resistive transitions, respectively. The observed improvement in properties is inferred to be largely associated with improved oxygen stoichiometry of the films although microstructural effects are not ruled out. © *1999 American Institute of Physics.* [S0003-6951(99)04819-6]

Perovskite manganites of the type $Re_{1-x}A_xMnO_3$ have received renewed interest since the discovery of colossal magnetoresistance (CMR) in these compounds.[1–4] The transport properties of these materials exhibit a transition from a paramagnetic insulating state to a ferromagnetic metallic state as the temperature is lowered. CMR materials are emerging as potential candidates for a variety of applications such as magnetic sensors, magnetic memories, etc. Besides these applications related to the colossal magnetoresistance, the sharp resistivity drop at the insulator–metal transition has recently been demonstrated to be very promising for uncooled IR detector (bolometric) applications.[5,6] In this letter, we demonstrate a significant enhancement in several characteristics of the CMR oxide thin films, particularly in properties relevant to the bolometric applications, which result from a modification of the material by the addition of Ag. A major concern, both in terms of fundamental understanding and applications, has been the existence of microscopic inhomogeneities, which affect the electrical and magnetic properties.[7] We observe that the addition of Ag leads to significant improvements in the electrical and magnetic homogeneity of thin films.

Thin films of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) were grown by pulsed-laser deposition on (100)-oriented $LaAlO_3$ substrates. The targets used for the deposition were prepared by the standard solid-state reaction method. Stoichiometric amounts of the powder were repeatedly ground and calcined at 1200 °C until phase purity was achieved. Subsequently, 5 wt % Ag was added before a final sintering of 1300 °C. Thin films were prepared from such Ag-added targets under a range of conditions and compared with films prepared from pristine targets without the Ag dopant. Henceforth, we will refer to Ag-added LCMO as ''Ag–LCMO'' and its pristine counterpart as ''LCMO.'' The structural quality of the films was studied by x-ray diffraction. dc resistivities were measured by the standard four-probe technique and the magnetization was measured using superconducting quantum interference device (SQUID) magnetometry. Ferromagnetic resonance (FMR) was used to study the magnetic homogeneity of the films. Film morphology was studied by atomic force microscopy (AFM).

The film deposition conditions[5] which yield the best LCMO films (i.e., energy density of 2.2 J/cm^2, oxygen partial pressure = 400 mTorr, and a substrate temperature (T_s = 820 °C) resulted in high-quality films of Ag–LCMO with somewhat better properties. The films are single phase and epitaxial as determined by x-ray diffraction studies. X-ray θ–2θ scans of the Ag–LCMO films are similar to that of pristine LCMO films except for a shift in the (001) peaks indicating a reduced c-axis lattice parameter. In Fig. 1 we showthe resistivity data of as-grown and annealed Ag–LCMO films. As-grown films of pristine LCMO, typically, have an insulator–metal transition temperature (resistivity

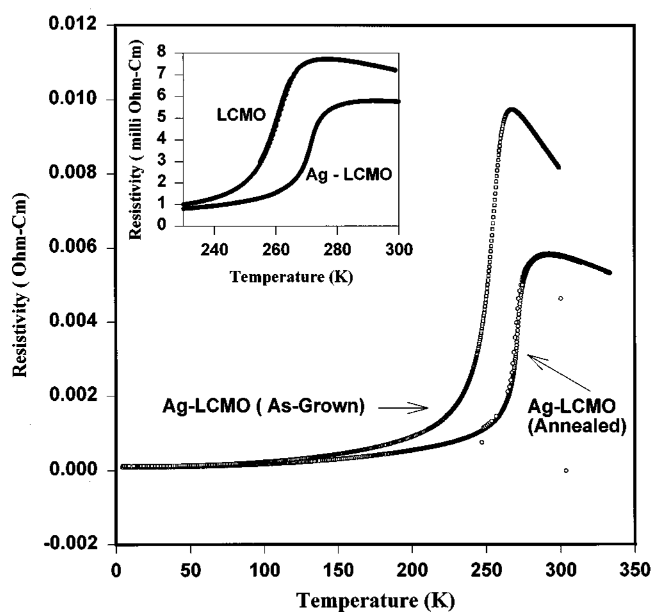

FIG. 1. Temperature dependence of resistivity for as-grown and annealed Ag–LCMO thin films. Inset shows the comparison between LCMO and Ag–LCMO annealed thin films.

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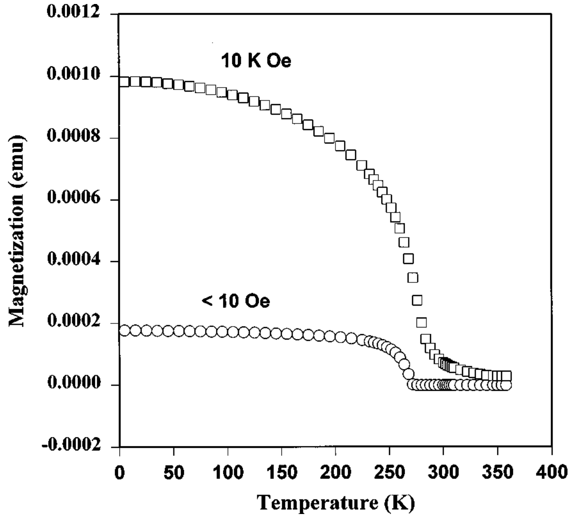

FIG. 2. dc magnetization data of the annealed Ag–LCMO thin film measured by SQUID magnetometer.

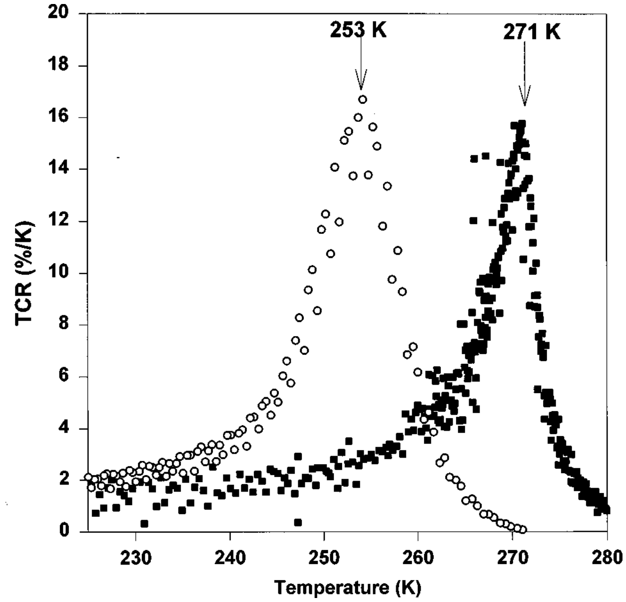

FIG. 3. Temperature coefficient of resistance (TCR) for annealed LCMO (○) and Ag–LCMO (■) thin films. Note that the TCR peak in the Ag–LCMO film occurs at a temperature 18 K higher than that of the pristine LCMO films.

peak temperature denoted as T_p) ~255–265 K; postannealing in oxygen (at 850 °C, 10 h) raises T_p to 275–280 K.[5] In Ag–LCMO films, the as-grown T_p is ~270 K. Annealing causes a dramatic improvement in the properties of Ag–LCMO films as compared to the best results on LCMO thin films. As shown in Fig. 1, in postannealed Ag–LCMO films we observe $T_p \sim 292$ K, bringing the metal–insulator transition in this material very close to room temperature. As shown in the inset of Fig. 1, the resistivities are significantly lower for the annealed Ag–LCMO films. dc magnetization measurements at low fields (shown in Fig. 2) indicate a ferromagnetic transition temperature $T_c \sim 270$ K in the annealed Ag–LCMO films, which is higher than that of annealed LCMO films, consistent with the higher T_p values in the former case. It may be noted here that the discrepancy between T_p and T_C (i.e., $T_p > T_c$) has been previously shown to be a characteristic of well-annealed thin films as well as high-quality single crystals.[8]

Along with the enhanced T_p and T_C, we observe that the resistivity transition becomes narrower on annealing. The width of the resistivity transition, characterized by the temperature coefficient of resistance (TCR), which is defined as $1/R\, dR/dT$, is a relevant figure for bolometric (infrared imaging) applications. Uncooled or moderately cooled IR imaging applications demand high values of TCR close to room temperature. In Fig. 3, we plot the TCR values of annealed films of Ag–LCMO where we observe TCR values ~16% at ~271 K. In the pristine LCMO films, the TCR is only ~<1% at this temperature; TCR values ~16% are obtained only at a lower temperature (253 K). This means that bolometric devices fabricated using the Ag-added LCMO thin films can operate at higher temperatures. An increase of the operating temperature by ~18 K is of substantial advantage in reducing the thermal load in IR imaging applications.[9]

Ferromagnetic resonance characteristics show significant changes on Ag addition. It has been observed previously[10] that thin films of the CMR materials show anomalous FMR characteristics. An ideal homogeneous ferromagnet is expected to show a narrow and temperature-independent FMR linewidth. In CMR thin films, FMR linewidths are often found to be large and temperature dependent, exhibiting a peak at T_c, and increasing as the temperature is lowered well below T_c. These characteristics are indicative of a distribution of T_c's and magnetization values in the sample. Particularly in LCMO, it has been found that as-grown films are magnetically inhomogeneous and the FMR signal is not observable. Annealing is known to make the films more homogeneous. However, even in the best annealed LCMO films to date, the linewidths are several hundreds of Oe for H perpendicular to the film plane (Γ_{perp}) and split into multiple lines below T_c. In contrast, as shown in Fig. 4, we observe that Γ_{perp} in annealed Ag–LCMO thin films is only ~40 Oe. To the best of our knowledge, this is the lowest value observed in LCMO films so far and is comparable to the best values obtained in $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) films. Even more significant is the fact that the observed linewidths are temperature independent at temperatures below T_C. This feature is

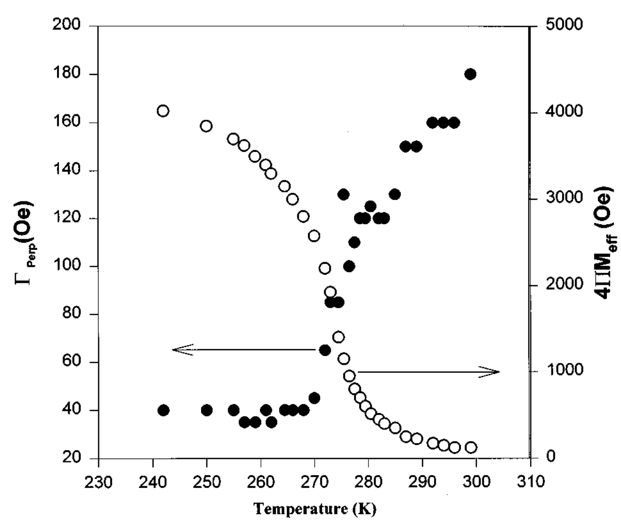

FIG. 4. Ferromagnetic resonance (FMR) characteristics of annealed Ag–LCMO thin films. FMR linewidths (Γ_{perp}) with field perpendicular to film plane as well as effective magnetization obtained from FMR are shown.

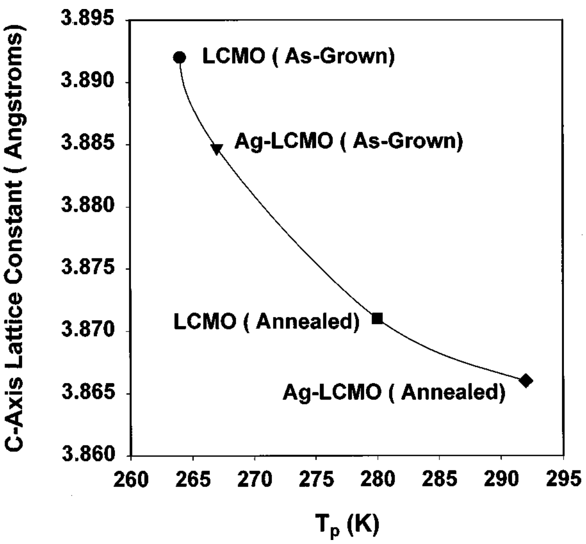

FIG. 5. *C*-axis lattice constants as a function of resistivity peak temperature in as-grown and annealed LCMO and Ag–LCMO thin films.

characteristic of a homogeneous ferromagnet. The FMR characteristics thus clearly indicate that the addition of Ag significantly improves the magnetic homogeneity of the films.

At this point, it is worthwhile to recall that addition of Ag to the high-temperature superconducting material $YBa_2Cu_3O_7$ (YBCO) has been known to lead to improvements in grain size, critical current densities, microwave properties, etc.[11–14] The effect of Ag addition in that case is understood to be partly due to a catalytic effect promoting grain growth during the film formation. Also, Ag is known to segregate at the grain boundaries, enhancing the grain-boundary conductivity. In addition, it is known that Ag forms oxides of Ag (Ag_2O) in the laser-generated plasma plume which decompose at the high temperatures near the substrate surface. This contributes to increased oxygen incorporation in the films due to the availability of nascent atomic oxygen.[11,14] In the present case, we have reason to believe that such oxygenation effects may be the key factor that leads to the observed improvements in properties. Previous work[7] has clearly established that there is a clear correlation between the oxygen content in the films, the electrical homogeneity (as indicated by the TCR values), magnetic homogeneity (as indicated by FMR linewidths), and higher values of the metal–insulator transition temperature (T_p) and the ferromagnetic transition temperature (T_c). Since oxygen content in thin films is nearly impossible to quantify by standard techniques such as thermogravimetry or iodometric titrations (due to the small film mass), we have examined structural changes to infer variations in the oxygen content. Previous results[15] on bulk materials and thin films have established the correlation between the *c*-axis lattice parameter and oxygen stoichiometry, where increase in oxygen content results in reduction of the *c*-axis lattice parameter. In Fig. 5 we show the *c*-axis lattice parameters as a function of T_p for as-grown and annealed LCMO and Ag–LCMO films. We see that enhancement of T_p is accompanied by a reduction of the *c*-axis lattice constant, which is smaller in the Ag-added LCMO films, suggesting a higher oxygen content. While the dominant influence may be related to the increase in oxygen stoichiometry, changes in microstructure (enhancement in grain size), or the effects of Ag segregation in grain boundaries may also contribute to the observed changes.

In conclusion, we have shown that addition of 5 wt % Ag to the LCMO target leads to significant improvements in several desirable properties of the thin films prepared by pulsed-laser deposition. In particular, we observe that the ferromagnetic transition and the metal–insulator transition occur at higher temperatures compared to the best pristine LCMO thin films. Both the electrical and magnetic homogeneity of the samples is also improved as indicated by high TCR values and narrow FMR linewidths. The enhancement of properties may be explained as partly due to the increase in oxygen content of the films, possibly due to the availability of nascent oxygen by decomposition of oxides of Ag.

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