CMR-Thin Films II Chang Beom-Eom, Chairman

Substrate, annealing, and Mn excess effects on La–Ca–MnO_3 thin films grown by metalorganic chemical vapor deposition: A way to room-temperature T_c

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Oriented thin films of the La–Ca–MnO_3 system with several Mn-excess compositions were prepared by aerosol-assisted metalorganic chemical vapor deposition. Depositions both on MgO (100) and $LaAlO_3$ (100) substrates were performed at temperatures between 700 and 800 °C, with 30 min *in situ* oxygen annealing at the deposition temperature. The films deposited on $LaAlO_3$ have much better structural quality with rocking curves of 0.3–0.7 full width at half maximum and higher T_c. For films with Mn excess, an *ex situ* annealing (800 °C for 1 h in flowing oxygen) increases T_c dramatically, from 180–190 K to values in the range 240–296 K, above the maximum T_c of the stoichiometric, optimally doped $La_{0.67}Ca_{0.33}MnO_3$ composition. This behavior may be associated with the presence of La vacancies, which act as self-dopants, and whose role is enhanced after suitable annealing. The films present high magnetoresistance values in the vicinity of the critical temperatures: at 7 kOe, 32% for a film with $T_c = 279$ K and 13% for a film with $T_c = 296$ K. The magnetic properties of the films on MgO were degraded by annealing, probably due to Mg diffusion to the film. © *1999 American Institute of Physics.* [S0021-8979(99)49708-7]

I. INTRODUCTION

Metalorganic chemical vapor deposition (MOCVD) is very versatile for complex oxide ceramic thin-film preparation, like HT_c superconductors and manganites with colossal magnetoresistance (CMR).[1–3] This technique allows the deposition on large nonplanar areas, useful for industrial purposes. The CMR properties of manganites are based on the mixed valence character of the Mn ions (Mn^{3+}/Mn^{4+}) and are strongly correlated to lattice distortions. The antiferromagnetic insulator $LaMnO_3$ compound can be doped with divalent La substitutions, leading to ferromagnetic metal-like behavior. Studies on $La_{1-x}Ca_xMnO_{3-\delta}$ thin films have focused on the optimal $x = 0.33$ composition with maximum $T_c = 267$ K. Electrical and magnetic properties were correlated to epitaxy, crystallinity, and oxygen content.[4] Recently, self-doped La-deficient $La_xMnO_{3-\delta}$ thin films prepared by pulsed laser deposition[5] and MOCVD (Ref. 6) were also shown to exhibit a CMR effect, with T_c near 300 K after suitable annealing.

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II. EXPERIMENT

La–Ca–$MnO_{3-\delta}$ thin films were prepared in an aerosol-assisted MOCVD reactor.[7] Organometallics precursors $Mn(tmhd)_3$, $La(tmhd)_3$, and $Ca(tmhd)_2$, were synthesized from tmhd (2,2,6,6-tetramethyl-3,5-heptanedione) and dissolved in bis(2-methoxyethyl)ether. The solution was ultrasonic nebulized at 810 kHz to produce an aerosol with 3 μm mean-particle diameter. Argon was used as a carrier gas and heated at 270 °C to volatilize both solvent and organometallics. Preheated oxygen was mixed just below the substrates which were induction heated with a stainless-steel susceptor. The melting points of KCl (770 °C) and NaCl (801 °C) were used for thermocouple calibration in O_2+Ar flow.

La–Ca–Mn–O_3 thin films were simultaneously deposited on 5×5 mm^2 MgO (100) (LCMO/MgO films) and $LaAlO_3$ (100) substrates (LCMO/LAO films), for 15 min, at temperatures ranging from 700 to 800 °C, with 30 min *in situ* annealing at the deposition temperature under 1 bar of oxygen pressure. All samples were annealed simultaneously at 800 °C for 1 h in flowing oxygen.

TABLE I. Data for La–Ca–$MnO_{3-\delta}$ films on MgO and $LaAlO_3$ substrates: composition by SEM/EDS, deposition temperatures, T_c from low-field magnetization, and rocking curve FWHM of the (004) peak. Symbols:* no critical features were found; n.d.: not determined; asd: as-deposited; and ann: annealed.

Dep.	Composition	Dep. temp. (°C)	$T_{c\text{-asd}}-T_{c\text{-ann}}$ (K)	FWHM asd	FWHM ann
I-MgO	$La_{0.63}Ca_{0.15}MnO_3$	700	160–*	1.07	0.96
II	$La_{0.55}Ca_{0.09}MnO_3$	750	135–150	1.23	1.13
III	$La_{0.90}Ca_{0.22}MnO_3$	720	*–180	n.d.	n.d.
IV	$La_{0.79}Ca_{0.08}MnO_3$	750	147–89	1.37	1.23
V	$La_{0.77}Ca_{0.20}MnO_3$	800	181–120	1.02	1.18
I-LAO	$La_{0.63}Ca_{0.15}MnO_3$	700	181–258	0.40	0.43
II	$La_{0.55}Ca_{0.09}MnO_3$	750	185–296	0.71	0.60
III	$La_{0.90}Ca_{0.22}MnO_3$	720	140–122	0.59	0.37
IVa	$La_{0.79}Ca_{0.08}MnO_3$	750	180–273	0.26	0.47
IVb	$La_{0.79}Ca_{0.08}MnO_3$	750	193–279	0.49	0.44
V	$La_{0.77}Ca_{0.20}MnO_3$	800	180–240	0.28	0.27

III. RESULTS AND DISCUSSION

Chemical compositions of the LCMO/MgO films were determined by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) analysis. For each LCMO/LAO film the composition is assumed to be the same as that of the LCMO/MgO film deposited at the same time, as quantitative SEM/EDS analysis is disturbed by the presence of lanthanum in the $LaAlO_3$ substrate. Film characteristics for five depositions (I–V) on both substrates are presented in Table I. Rutherford backscattering spectroscopy (RBS) showed that sample thicknesses are approximately 150 nm. X-ray diffraction (Cu $K\alpha, \theta/2\theta$) show that all films grow with the *c* axis (Pbnm group) perpendicular to the substrate. LCMO/LAO films only presented (00*l*) peaks, while some LCMO/MgO presented a very small (200) peak, which decreases by annealing. On the as-deposited samples the *c*-axis value ranges from 7.727 to 7.769 Å, indicating the presence of elastic uniform strain due to the substrate. Detailed peak analysis shows nonuniform strain[8] (ϵ) up to 1% with higher values in the LCMO/MgO films. Samples II present the highest ϵ, probably due to the largest amount of vacancies. After annealing, strain relaxation is observed, the *c* axis decreases to values between 7.706 and 7.748 Å, and ϵ decreases to nearly 0.5%. The rocking curve full width at half maximum (FWHM) of the (004) peak is typically much narrower in LCMO/LAO than in LCMO/MgO and is not appreciably changed by annealing. The Scherrer equation gives the crystallite size perpendicular to the surface of the order of 30 nm for LCMO/LAO and 20 nm for LCMO/MgO.

SEM images of the polycrystalline microstructures of the deposition II films are shown in Fig. 1. Before annealing, the LCMO/LAO grains are square faced, with edges parallel to the substrate edges [Fig. 1(c)], while the LCMO/MgO grains do not present a uniform geometry [Fig. 1(a)]. The grain size is nearly 100–150 nm. After annealing, only minor modifications can be seen on LCMO/MgO [Fig. 1(b)], but sintering of LCMO/LAO occurs [Fig. 1(d)].

The temperature dependence of the magnetization (M) was measured in a magnetic field of 20 Oe, heating from a field-cooled state. Figure 2 represents the results of sample II and IV. Higher M is found in LCMO/LAO than in the LCMO/MgO films. Upon annealing, M is severely reduced on LCMO/MgO. In the as-deposited state, the critical temperatures (T_c defined by the minimum in dM/dT) in LCMO/LAO are generally higher than in LCMO/MgO (see Table I). Upon annealing, the T_c of LCMO/LAO has a maximum shift of 111 K upwards (sample II). On the other hand, the T_c of LCMO/MgO is decreased by annealing and the transition is broadened. In some cases, annealed LCMO/MgO do not show a magnetic transition at all. We remark that for sample V the as-deposited T_c's were the same (180 K) but they strongly differ after annealing. These different behaviors may be due to Mg diffusion to the film surface after annealing, confirmed by RBS analysis. On the LCMO/LAO samples no Al diffusion was found.

High-field magnetization at 10 K of sample II-LCMO/LAO, gives saturation fields of 6 and 1.5 kOe and saturation

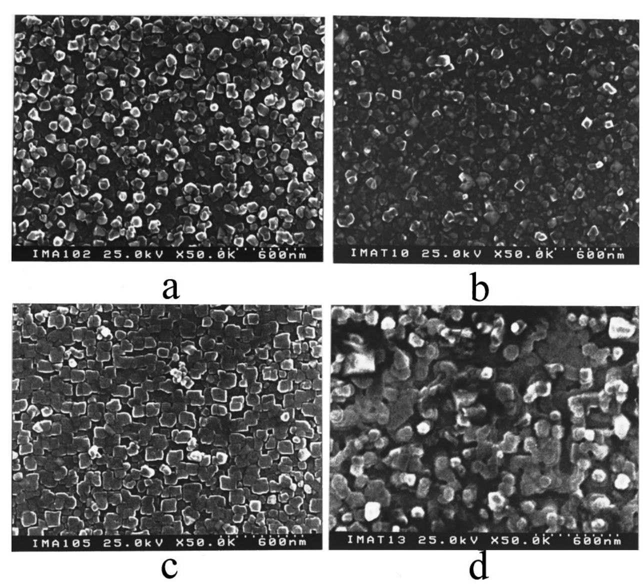

FIG. 1. SEM images of $La_{0.55}Ca_{0.09}MnO_3$ films (deposition II). Legend: (a): LCM/MgO as deposited; (b): LCMO/MgO annealed; (c): LCMO/LAO as deposited; and (d): LCMO/LAO annealed. LCMO/LAO films have larger grains.

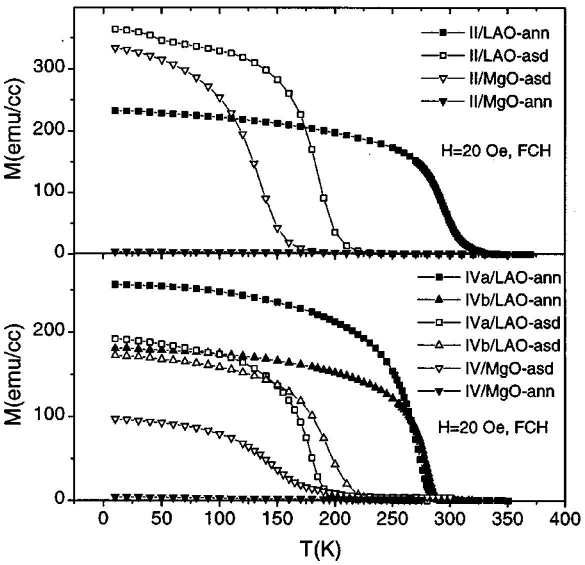

FIG. 2. Low-field magnetization of as-deposited and annealed films II and IV on MgO and $LaAlO_3$.

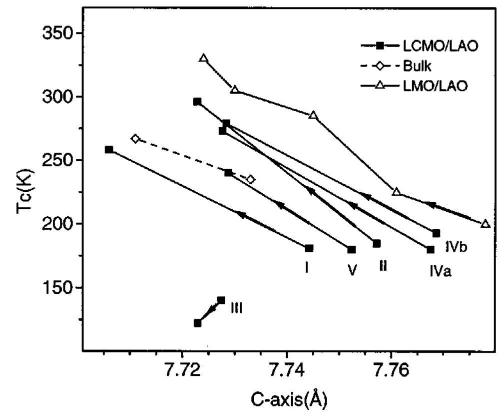

FIG. 4. Effects of oxygen annealing on the critical temperature and *c*-axis length of the films deposited on $LaAlO_3$. Lines with arrows (←) connect the as-deposited to the annealed samples. Data from Ref. 6 on subsequent annealings on $La_{0.8}MnO_{3-\delta}$ films (LMO/LAO, different criterium for T_c, see the text) and for two bulk samples are included. Sample III is Mn deficient. T_c increase upon annealing on the LCMO/LAO samples with Mn excess correlates to the reduction of the *c*-axis length.

magnetizations of 430 and 550 emu/cm^3, respectively, before and after annealing. Coercive fields at 10 K decrease from 300 to 150 Oe. Figure 3 shows the electrical resistivity of sample II-LCMO/LAO before and after annealing, confirming the shift of the metal–insulator transition to room temperature. The increase of resistivity at low temperatures after annealing may be associated with the more irregular grain structure shown in Fig. 1(d). Annealed LCMO/LAO present high magnetoresistance $\Delta\rho(H)/\rho$ values near T_c: at 7 kOe, 32% for film IVa with $T_c = 279$ K, and 13% for film II with $T_c = 296$ K. The temperature dependences of the $\Delta\rho/\rho$ and of the temperature derivative $d\rho/dT$ have very similar shapes (see the inset of Fig. 3).

A correlation between the *c*-axis length and the changes of T_c values due to annealing is represented on Fig. 4 for the LCMO/LAO samples with Mn excess: an increase of T_c corresponds to a reduction of the *c*-axis length. In addition, we remark that the lines connecting the as-deposited to the annealed samples have almost parallel slopes. Pignard *et al.*[6] studied the annealing effect on $La_{0.8}MnO_3$ MOCVD thin films deposited on $LaAlO_3$ (LMO/LAO). Their data correlate in a similar way the increase of T_c (from magnetization measurements at 2 kOe) to the *c*-axis length reduction with subsequent annealings from 600 to 800 °C. In Fig. 4 we also present data for two $La_{1-x}Ca_xMnO_3$ bulk compounds ($x = 0.25$, $T_c = 235$ K and $x = 0.33$, $T_c = 267$ K) with Mn/(La+Ca)=1 ratio (dotted line), for which the mixed valence Mn^{3+}/Mn^{4+} ratio is related to the *c*-axis length.[9] The LCMO/LAO film with Mn/(La+Ca)≈1 (deposition V, $La_{0.77}Ca_{0.20}MnO_3$) has T_c and *c*-axis length close to the bulk sample of nearly identical composition. Film III, which does not follow the correlation and where T_c decreases by annealing, is Mn deficient ($La_{0.90}Ca_{0.22}MnO_3$). This allows the conclusion that in the La–Ca–Mn–O system T_c can be enhanced either by annealing (oxygen incorporation and strain relaxation) or by increasing the Mn/(La+Ca) ratio. T_c near room temperature with a considerable CMR effect was obtained in LCMO/LAO films by combining these effects.

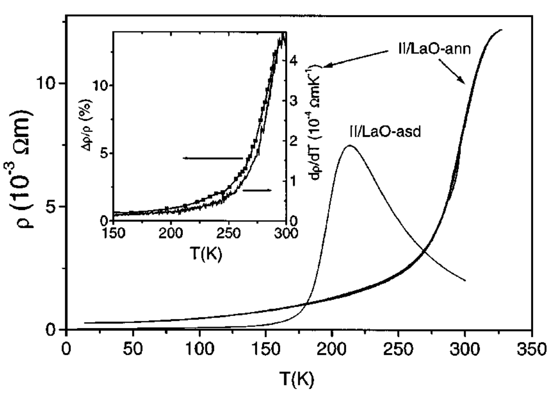

FIG. 3. Electrical resistivities (ρ) of films II on $LaAlO_3$ as deposited and annealed. Inset: magnetoresistance $\Delta\rho/\rho$ at 7 kOe and $d\rho/dT$ for the annealed film.

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