Influence of the Deposition Parameters on La−A−Mn−O (A = Ca, Sr) Films Grown by Low-Pressure Aerosol Pyrolysis

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Thin films of composition $La_{1-x}A_xMnO_3$ (A = Ca, Sr) were deposited by a modified CVD process. This method uses pyrolysis of an aerosol obtained by high-frequency spraying of a solution containing the corresponding 2,2,6,6-tetramethylheptane-3,5-dione complexes solved in diethylene glycol dimethyl ether. The growth was carried out at different temperatures in an oxygen/argon atmosphere at a constant pressure of 10 Torr. The influence of the deposition parameters on the growth of ferromagnetic films, either without any preferential orientation or highly [100] oriented, is analyzed.

Introduction

Oxide films with the perovskite structure and formula $La_{1-x}A_xMnO_3$, where A is a divalent ion, are ferromagnetic over a wide compositional range and have been shown to exhibit a giant magnetoresistance (MR) effect.[1,2] The very large MR observed in these materials has attracted much recent attention because of their potential application in information storage and other magnetic field sensing devices.

Although the mechanism of the MR effect is not completely understood so far, it is known that one of the MR mechanisms is based on the mixed-valence character of the Mn ion (Mn^{3+}/Mn^{4+}) through the double exchange between both ions.[3−5] In the case of the undoped material $LaMnO_3$, it is an antiferromagnetic insulator, but the substitution on La^{3+} sites by an alkaline earth ion or introduction of lanthanum vacancies results in a mixed valence Mn^{3+}/Mn^{4+} state. In this sense, studies on $La_{1-x}Ca_xMnO_3$ system have focused on the optimal $x = 0.33$ composition,[6] as well as in self-doped La-deficient La_xMnO_{3-y} thin films which also exhibit a MR effect.[7]

The properties of these films are dependent on the conditions of growth, composition, possible substrate epitaxy, and the overall microstructure.[8] Different methods to prepare thin films of manganese oxides have been used, for instance, pulsed laser deposition,[7] RF magnetron sputtering,[9] molecular beam epitaxy,[10] sol−gel,[11] aerosol MOCVD,[12] metalorganic decomposition[13] and electrochemical deposition.[14]

The present paper tries to assess the conditions for optimal growth of $La_{1-x}A_xMnO_3$ (A = Ca, Sr) thin films by low-pressure aerosol pyrolysis, mainly with regard to those compositions which, according to the literature, show higher MR values. We report a further analysis of the influence of different deposition parameters on the main features of thin films prepared by this method.

Experimental Section

Thin films were prepared in the device shown in Figure 1. The apparatus consists of a gas flow control system, an aerosol generator, a pyrolysis zone, and a vacuum system. In this device, the precursor solution is transported as an aerosol, which is generated by ultrasonic excitation using a piezoelectric transducer. The pyrolysis zone is formed by a quartz reactor with an outer diameter of 50 mm, where two regions can be distinguished: a preheating zone, heated externally by a resistance, and a substrate holder on top of it, which is

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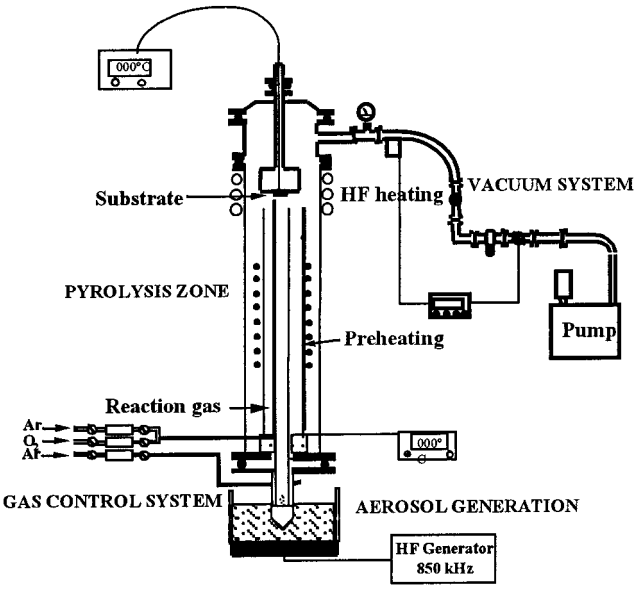

Figure 1. The aerosol−CVD setup used for the thin film preparation.

heated by using high-frequency induction. The substrate temperature is monitored by a thermocouple inserted into the stainless steel substrate holder. The vacuum system, which includes a Baratron linked to a butterfly valve allows one to work in a dynamic vacuum.

The aerosol is transported using Ar to the preheating zone of the reactor kept at 250 °C, where solvent and precursors are evaporated. This gas phase is then transported to the substrate, heated at temperatures between 650 and 900 °C, where a CVD reaction can take place. A mixture of oxygen and argon is used as reaction gas. To prevent any passage of condensable vapors, as well as to collect byproducts, a liquid nitrogen trap was placed between the pyrolysis zone and vacuum pump.

We have used 2,2,6,6-tetramethylheptane-3,5-dione (thd) complexes solved in diethylene glycol dimethyl ether as precursor solution refrigerated at $T = 10$ °C. The solvent has been chosen due to its physical properties, which allow generation of a high aerosol flow, and due to the good solubility of β-diketonates.[15]

The reactants $La(thd)_3$, $Ca(thd)_2 \cdot 2H_2O$, $Sr(thd)_2 \cdot 2H_2O$, and $Mn(thd)_3$ were prepared according to previously documented procedures, albeit slightly modified.[16] The characterization of these complexes by thermogravimetry, elemental analysis and infrared spectroscopy indicates the composition shown above.

For the thin film preparation, Si(100) and MgO(100) were used as substrates. The deposition temperature was varied between 650 and 900 °C and O_2/Ar mixture was used as reaction gas (300 sccm O_2/200 sccm Ar). In all cases, the films were deposited at a constant pressure of 10 Torr, higher than the vapor pressure of the solvent at 10 °C. The deposition time was 10 min, but to study the influence of this factor on thin film characteristics, in some experiments this time was varied between 2 and 20 min. After the deposition, the films were cooled to room temperature in oxygen atmosphere. The materials have not been postannealed after film deposition.

The films obtained were characterized by X-ray diffraction (XRD) in a Philips X-Pert MPD diffractometer equipped with a thin-film (grazing incidence) attachment and a flat monochromator placed between sample and detector and using Cu Kα radiation. The average thickness of the films was measured using X-ray interferometry. Surface morphology and film thickness were examined by Scanning Electron Microscopy (SEM) on a JEOL 6400 instrument. The cationic ratio of the films was determined by means of an Electron Probe Micro Analyzer (EPMA) attached to a JEOL JXA-8900M microscope. Specimens for cross-sectional TEM were prepared by standard ion milling method. The studies were carried out in a Philips TM200 electron microscope FEG equipped with an EDAX-DX4 analyzer. The magnetic susceptibility was measured in a SQUID (MPMS-5S QUANTUM DESIGN) magnetometer, with a temperature range between 5 and 350 K and an applied field of 0.1 T. The resistance measurements were carried out by the four-probe method by means of a system attached to the SQUID magnetometer, with field of 0−9 T and a temperature interval at 5−500 K.

Table 1. Concentration of Precursor Solution Used To Generate the Aerosol, Cationic Ratio, and Composition of Deposited La−A−Mn−O (A = Ca, Sr) Films

concentration of precursor solution (mM)			film cationic ratio		
$[La(thd)_3]$	$[A(thd)_2]$	$[Mn(thd)_3]$	La/Mn	A/Mn	film composition
10		10	0.7		$La_{0.7}MnO_{3-y}$
15		10	0.45		Phase Mixture
11.5		10	0.8		$La_{0.8}MnO_{3-y}$
5		5	No deposition		
6.6	3.3	10	0.55	0.07	$La_{0.55}Ca_{0.07}MnO_{3-y}$
8.5	10	10	0.7	0.2	$La_{0.7}Ca_{0.2}MnO_{3-y}$
8.5	14	10	0.7	0.3	$La_{0.7}Ca_{0.3}MnO_3$
8.5	14	10	0.5	0.5	$La_{0.5}Sr_{0.5}MnO_3$

Results and Discussion

The stoichiometry of the film is a very important factor for both La−Mn−O and La−(Ca,Sr)−Mn−O systems. The stoichiometry determines the phase composition and, as a consequence, the magnetoresistive properties of the films.[17,18] In the experimental setup used for thin-film deposition the control of the precursor solution composition should allow the composition of the film to be modified, since the characteristics of the precursor solution (employed precursor, concentration, viscosity) affect the nature of the generated aerosol and, in consequence, the composition of the obtained film. In this sense, the solution concentration and the cationic ratio were varied to study the effect of such changes in the film composition, and to obtain films with the desired composition.

Table 1 shows the results of some experiments carried out. As a general trend, it can be observed that the La/Mn ratio in the film is always slightly lower than in the solution, i.e., the deposition rate was greater for $Mn(thd)_3$ than for $La(thd)_3$ and led to a La-to-Mn ratio in the film lower than in the solution. If the La concentration on the solution was high, the La/Mn ratio on the film decreased. Besides, hardly any deposit was obtained when working with total solution concentration significantly lower than 20 mM. Thus, to obtain $La_{1-x}MnO_{3-y}$ films, the total solution concentration must be kept close to 20 mM, and slight modifications of La concentration led to films with different x values. On the other hand, the inclusion of alkaline earth complex into the solution modifies the deposition rate of those previous precursors. According to the above results, and to obtain films with the composition

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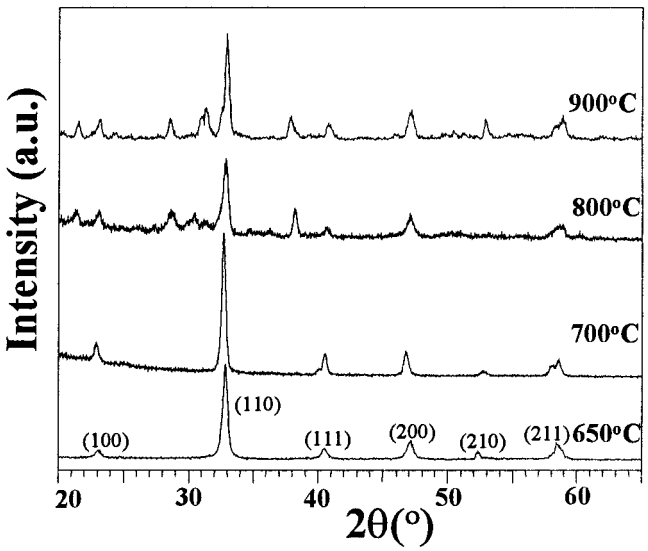

Figure 2. 2θ scan XRD patterns at fixed incidence angle $\theta = 1°$ for thin films grown at different temperatures during 10 min on Si(100) substrate.

$La_{2/3}Ca_{1/3}MnO_3$, the La and Mn solution concentrations were kept close to 20 mM, and different concentrations of $Ca(thd)_2$ were used. The results collected in Table 1 show that the calcium is poorly transported into the film, but lanthanum is transported better than in absence of calcium. For each system, a relationship between precursor solution composition and film composition is obtained. Therefore, it is necessary to adjust the characteristics of the precursor solution for each system to obtain the desired stoichiometry on the thin film. No significant differences in composition were observed as a function of the deposition temperature or substrate.

Taking into account the results obtained, it can be stated that under the experimental conditions above explained the manganese is transported into the films better than lanthanum, which in turn is better transported than calcium or strontium. On the other hand, lanthanum complex is transported better when calcium is present in the solution. The lower alkaline earth content in the film relative to solution was previously observed in other systems such as Sr−Fe−Co−O[19] or Y−Ba−Cu−O[20] and could be related to $A(thd)_2$ oligomer formation in the solid precursor aerosol particles or in the gas phase.[21,22]

The influence of substrate temperature on the film characteristics was also studied. All the films deposited were mirrorlike in appearance. When Si(100) was used as substrate, the $\theta - 2\theta$ XRD patterns of the films show predominantly the Si(100) Bragg reflection which is accompanied by other weak peaks corresponding to perovskite phase. As the Bragg peaks showed no specific orientation dependence in $\theta/2\theta$ scans, a 2θ scan was performed at a fixed θ angle (1°) to remove the Si Bragg reflection. Figure 2 shows the XRD patterns of La−Mn−O samples prepared at different temperatures. Similar results were obtained when Ca or Sr were introduced into the films. The XRD patterns of films synthesized at 650 and 700 °C show a single phase, with patterns similar to those of a cubic perovskite structure without any splitting of (h00) or (hh0) reflections. However, at higher temperatures, we can see other diffraction maxima together with those maxima corre-

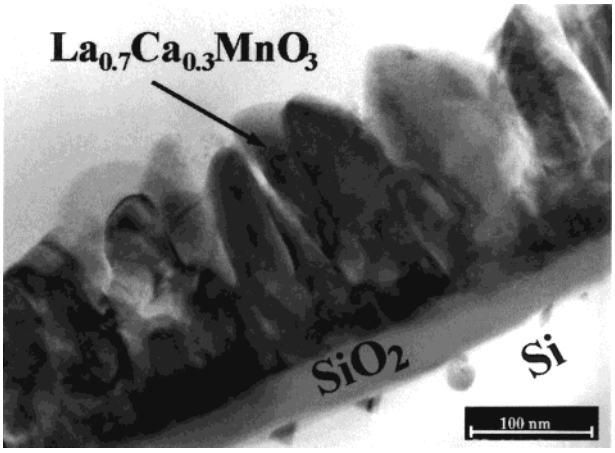

Figure 3. Cross-sectional TEM micrograph of $La_{0.7}Ca_{0.3}MnO_3$ film deposited at 700 °C (20 min) onto Si(100).

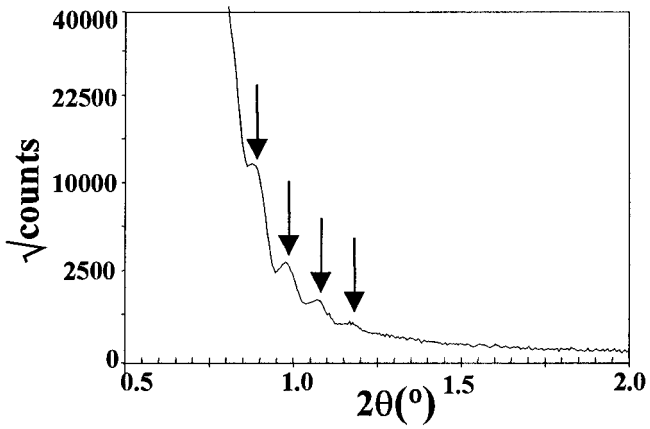

Figure 4. Interference pattern of $La_{0.7}MnO_{3-y}$ film deposited at 700 °C (10 min) onto Si(100).

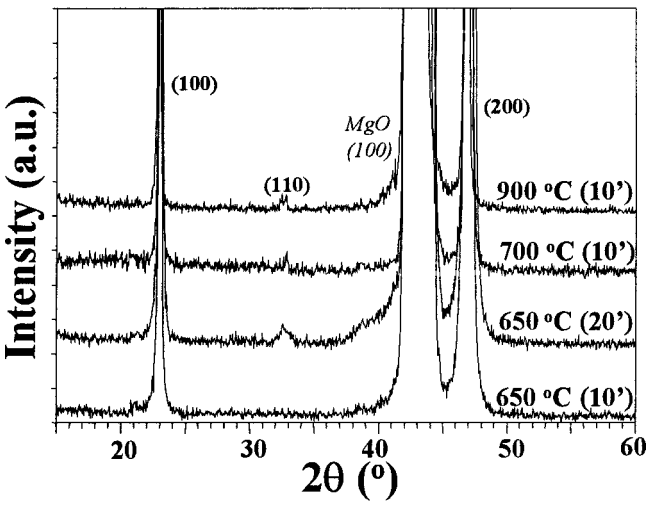

Figure 5. $\theta - 2\theta$ scan XRD patterns of $La_{0.7}MnO_{3-y}$ thin films deposited on MgO substrate.

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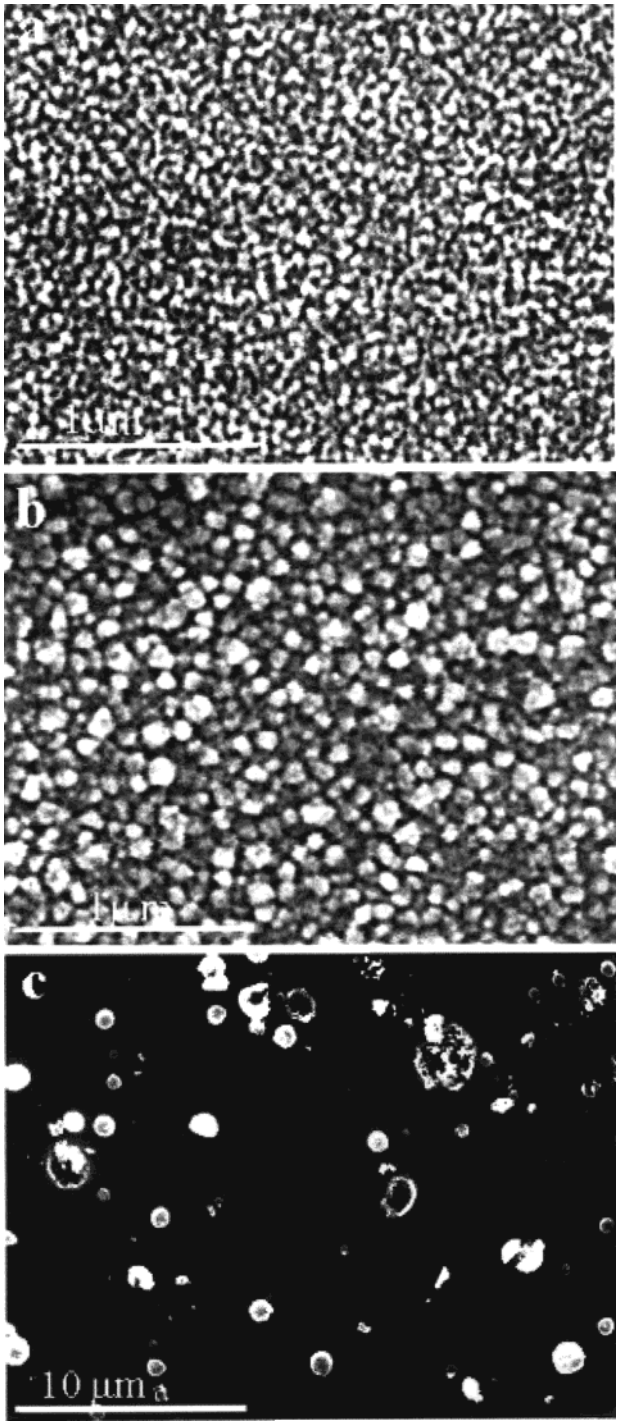

Figure 6. SEM micrographs of $La_{0.7}Ca_{0.3}MnO_3$ films deposited during 10 min on Si(100) at different temperatures: 650 °C (a), 700 °C (b), and 750 °C (c).

sponding to perovskite phase. As will be discussed below, these maxima, not attributable to a perovskite structure, were not observed when working with MgO substrates; therefore, and although it is difficult to arrive to an unequivocal phase identification on the basis of these unknown maxima, they could correspond to a silicate phase formed by a reaction of the precursor at high deposition temperature with the silicon substrate, as previously observed in the La−Al−O system.[23,24] Thus, it is possible to obtain a crystalline single perovskite phase onto Si substrates, without an ulterior thermal treatment, if the deposition temperature is kept below $T = 700$ °C.

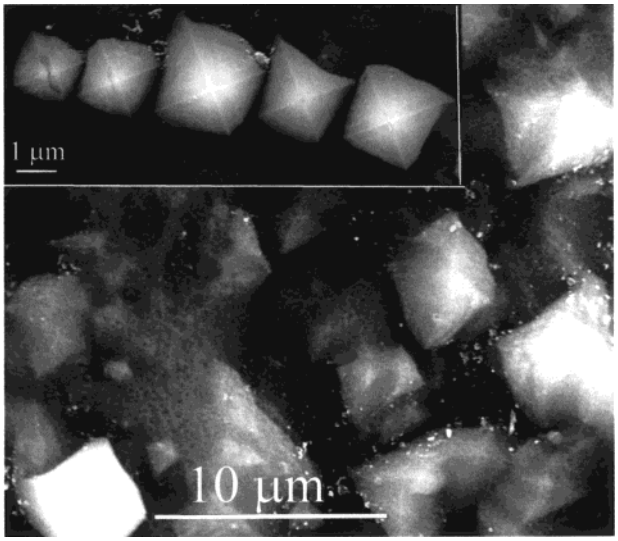

Figure 7. SEM micrograph of $La_{0.7}MnO_{3-y}$ film deposited at 650 °C (10 min) onto MgO(100). The inset shows the shape of the crystals in greater detail.

The single-phase films deposited onto Si(100) were analyzed by TEM. Figure 3 shows a cross-sectional TEM micrograph of $La_{0.7}Ca_{0.3}MnO_3$ film deposited at 700 °C (20 min). The cross-sectional analysis of the films showed the formation of a SiO_2 thin layer between the perovskite phase and the Si substrate. This SiO_2 layer was amorphous as observed by electron diffraction. This amorphous interlayer could justify the polycrystalline character without preferential orientation of perovskite films deposited onto these Si substrates.

The thickness of films deposited onto Si(100) was measured using X-ray interferometry. The difference between the angular positions of these low-angle reflections allows the thickness of the deposited films to be estimated. Figure 4 shows the interference pattern corresponding to $La_{0.7}MnO_{3-y}$ deposited onto Si(100) at 700 °C during 10 min. The drop in intensity over the observed fringes gives an idea of a substantial interface roughness. This effect is the main limiting factor in the obtaining of interferometry scan of films deposited by pyrosol technique. The approximate thickness calculated using X-ray interferometry was of 50 nm at 650 °C and 90 nm for the film deposited at 700 °C, with a deposition time of 10 min in both cases. That means that the growth rate varied between 5 and 9 nm/min as a function of temperature. The deposition rate obtained working at low pressure is much higher than the one observed in films deposited using this method but at atmospheric pressure.[24]

Figure 5 shows the $\theta/2\theta$ XRD patterns of $La_{0.7}MnO_{3-y}$ films deposited onto MgO at different temperatures. All the XRD patterns show intense diffraction maxima corresponding to (h00) reflection of perovskite phase together with intense maxima corresponding to MgO substrate. It is then possible to obtain a single perovskite phase, using MgO as substrate, in the whole temperature range (650−900 °C). These results seem

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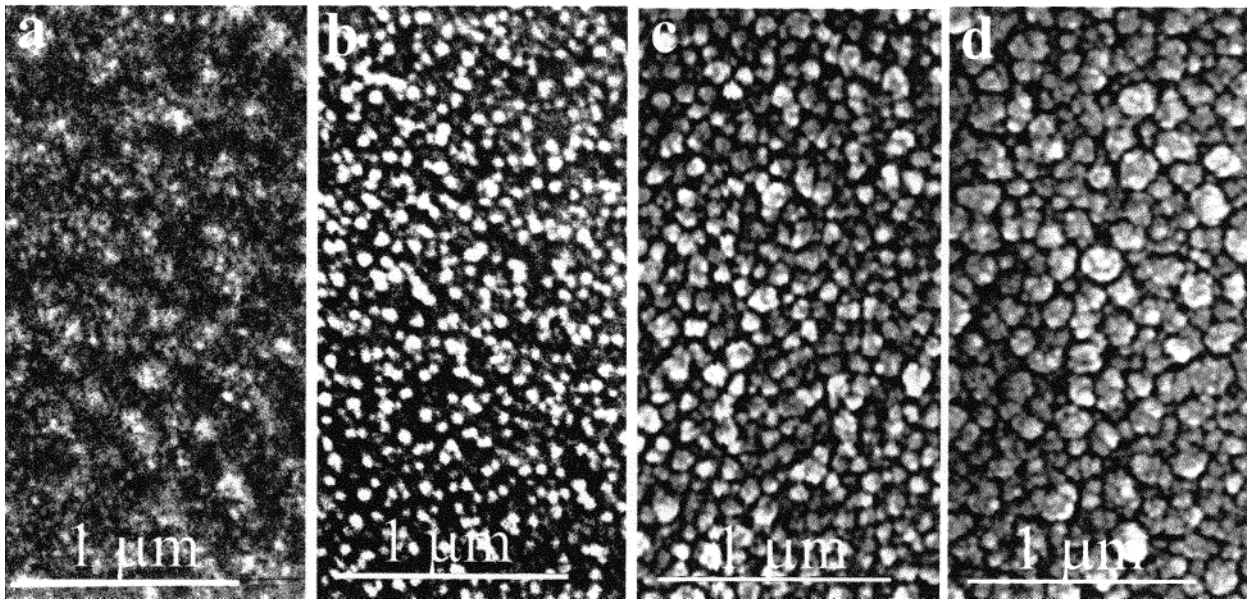

Figure 8. SEM micrographs of $La_{0.7}Ca_{0.3}MnO_3$ thin films obtained at 700 °C on Si(100) at different deposition times: 2 min (a), 5 min (b), 10 min (c), and 20 min (d).

to confirm the high-temperature reaction of the precursors with the silicon substrate discussed above. On the other hand, the MgO substrate allows the film to grow in a [100] preferential direction, that is, the substrate interaction for perovskite preferential growth is more favorable when MgO is used instead of silicon. However, the XRD study reveals that when the temperature or deposition time were increased, the (110) maxima of perovskite phase also appear on the film XRD patterns. This fact could be related with the increase in thickness when the temperature or deposition time increase, and the difficulty in obtaining oriented films for high thicknesses.[25,26]

The comparison of surface morphology of $La_{0.7}Ca_{0.3}MnO_3$ films grown at different temperatures onto Si (100) is shown in Figure 6. The SEM micrographs show a homogeneous surface on films deposited at 650 and 700 °C (Figure 6a,b), which appears to be constituted by small crystals, whose grain size evolves with the temperature. However, at higher temperatures, and although the films seem mirrorlike in appearance, the SEM micrograph shows an inhomogeneous surface (Figure 6c), where big particles and the formation of voids on the film surface can be observed. By taking into account the results observed in the XRD pattern for this temperature, which indicate the presence of another phase together with the perovskite, the inhomogeneities in the film could be due to this fact. The film thickness, measured on SEM fracture micrographs, varies between 60 and 110 nm for films deposited for 10 min at 650 and 700 °C, respectively, in accordance with the results obtained by X-ray interferometry.

The surface morphology of films deposited onto MgO is very different to that observed when Si is used as substrate. Then, the SEM micrograph shown in Figure 7, corresponding to $La_{0.7}MnO_{3-y}$ grown at 650 °C during 10 min, shows that the film is constituted by big crystals of 3−4 μm of size. These crystals have a preferential orientation, in agreement with the XRD data, but the films show poor grain coupling. Similar results were observed when Ca or Sr were introduced.

According to Jin et al.[27] the magnetoresistance of the films is affected by their thickness. In our device, this parameter can be also controlled by varying the deposition time. Figure 8 shows the evolution of film microstructure as a function of the deposition time, the deposition temperature being 700 °C. Figure 8a shows that for a deposition time of only 2 min, the substrate is already covered by a thin film of small $La_{0.7}Ca_{0.3}MnO_3$ crystallites. As the deposition time increases the size of these crystals also increases (Figure 8b−d). Therefore, this grain growth could be related to the increase in film thickness for higher deposition times; deposition times of 10 and 20 min give rise to 100- and 200-nm-thick films, respectively.

On the other hand, the film composition plays a role in the microstructure of the films. Figure 9 shows the surface of films, grown in the same experimental conditions, with different composition. These SEM micrographs show that the grain size increases when Ca/Sr are present and the grain shape is also changing as a function of film composition.

A preliminary study on some films suggests a ferromagnetic behavior as observed in Figure 10, which depicts the variation of magnetic susceptibility versus temperature for films deposited at 700 °C (10 min) onto Si(100) with different compositions. The magnetic transition temperature, T_c, defined as the temperature of the minimum in the $d\chi/dT$ curve, varies between 170 and 350 K depending on the film composition. The T_c values observed for doped samples, 173 K, corresponding to $La_{0.7}Ca_{0.3}MnO_3$ sample, and 337 K, for $La_{0.5}Sr_{0.5}MnO_3$, are similar to those obtained by other authors on thin films prepared using other deposition meth-

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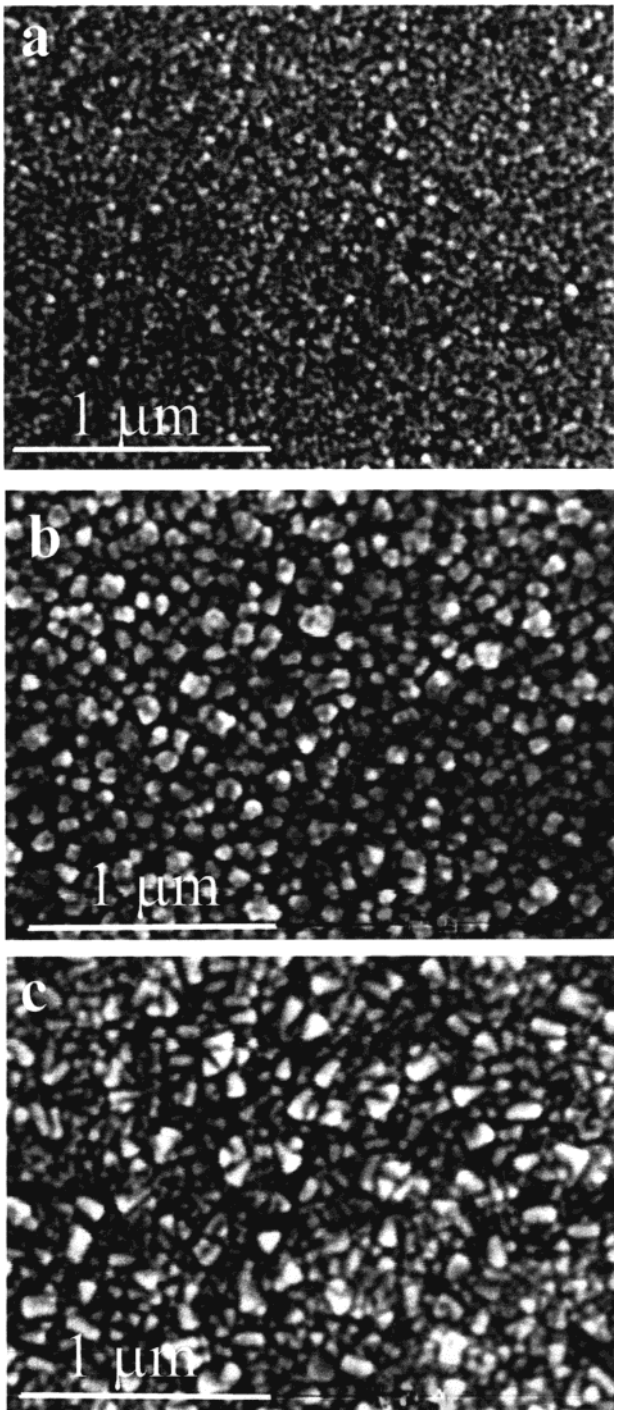

Figure 9. SEM micrographs corresponding to $La_{0.7}MnO_{3-y}$ (a), $La_{0.7}Ca_{0.3}MnO_3$ (b), and $La_{0.5}Sr_{0.5}MnO_3$ (c) films deposited at 700 °C (10 min) on Si(100).

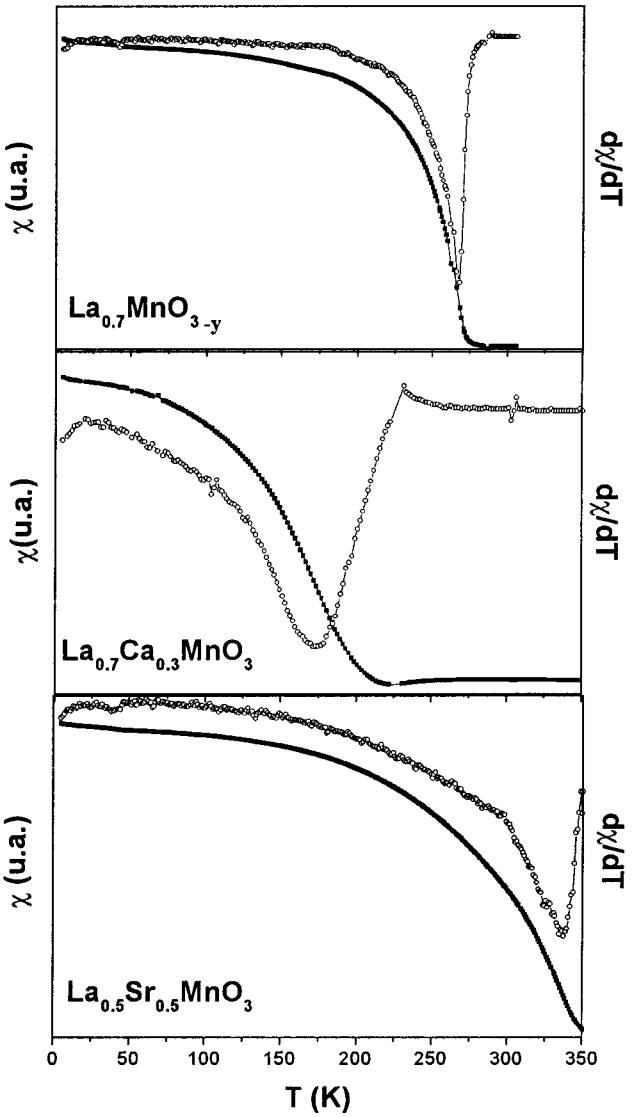

Figure 10. Magnetic susceptibility and dχ/dT versus temperature of La−A−Mn−O films deposited at 700 °C (10 min) on Si(100).

ods[28,29] although slightly lower than those observed in bulk samples.[6,30] The magnetic transitions of the films are broader than those of the bulk materials, which could indicate that the films are less homogeneous.[28] On the other hand, we emphasize the high concentration of La vacancies (30%) observed in the undoped sample, $La_{0.7}MnO_{3-y}$, with a T_c close to 270 K. This La vacancy concentration has been only observed in thin films,[31] whereas in powder samples the maximum vacancy concentration, while maintaining the ferromagnetic behavior, is approximately 20%.[32,33] Besides, the different electric resistance value of $La_{0.7}Ca_{0.3}MnO_3$ deposited onto Si (100) at 700 °C during 10 min, under zero applied magnetic field (R_0) and under applied field (R_H) gives rise to a magnetoresistive (MR) behavior, defined as: $MR = [(R_0 - R_H)/R_0] \times 100$, with MR values close to 60% for $H = 9$ T and 5 K (Figure 11).

Conclusions

A simple and versatile solution method is used to prepare "in situ" $La_{1-x}A_xMnO_3$ (A = Ca, Sr) thin films onto different substrates without need of an ulterior

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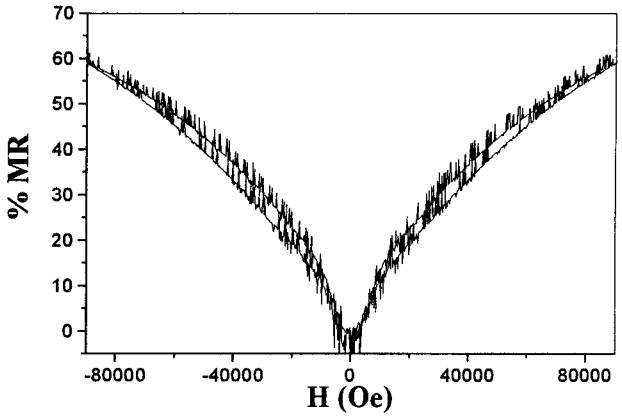

Figure 11. Magnetoresistance (MR) percentage versus magnetic field at 5 K for the $La_{0.7}Ca_{0.3}MnO_3$ film deposited at 700 °C (10 min) on Si(100).

thermal treatment. By modifying the deposition parameters, films with different composition, particle size- and thickness can be obtained. The films deposited on Si(100) were polycrystalline without any preferential orientation, probably due to the formation of an amorphous SiO_2 layer between the substrate and the manganese oxide. However, when MgO(100) is used as substrate, the substrate interaction for perovskite preferential growth is favored, then well [100] oriented perovskite films can be obtained by controlling the temperature and deposition time. The films deposited by low-pressure aerosol pyrolysis show a ferromagnetic behavior with transition temperature depending on the film composition and a MR value close to 60% for $La_{0.7}Ca_{0.3}MnO_3$.

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