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$La_{1-x}MnO_{3-\delta}$ thin films grown by a new liquid source CVD process

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Abstract

A new liquid source CVD process has been developed in order to control precisely the amount of organometallic precursor vapours to be produced. Using this technique, thin films of self-doped $La_{1-x}MnO_{3-\delta}$ have been deposited on MgO (100) and $LaAlO_3$ (012) single crystals with various x values: $x = 0$, 0.06, 0.09, 0.20 and 0.25. X-ray diffraction measurements reveal an epitaxial growth on the two kinds of substrates. The as-deposited films exhibit ferromagnetic transitions at various temperatures depending on the x value. Different electrical behaviours are observed depending on x. A semiconductor/metal transition is obtained for samples with the highest x value. Magnetoresistance of the most lacunar as-deposited film has been measured: a GMR effect of 25% per tesla (T) is obtained at 190 K. © 1997 Elsevier Science S.A.

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1. Introduction

Lanthanum manganese oxides, with the general formula $La_{1-x}A_xMnO_{3-\delta}$ where A is a substituting cation, are of great interest because of the giant magnetoresistive (GMR) properties obtained when $x > 0.1$. The potential applications of such properties are as magnetoresistive heads for high-density magnetic recording [1] and as magnetic sensors [2].

These compounds, where A is generally a divalent cation [3–6] (A = Ca, Sr, Ba, Pb) or more rarely a monovalent one [7,8] (A = Ag, K, Rb), are known to exhibit a paramagnetic/ferromagnetic transition (temperature T_C) and a semi-conductor/metal transition (temperature t_ρ) with, generally, t_ρ close to T_C. Indeed the substitution of lanthanum by cations of lower valency maintains the perovskite structure and induces a mixed valency of manganese (Mn^{3+} and Mn^{4+}) responsible for the magnetic double-exchange and thus for magnetoresistive properties.

Despite their interest, there have only been a few reports in the literature on lacunar lanthanum manganite thin-films of general formula $La_{1-x}MnO_{3-\delta}$. Vacancies on the lanthanum site induce mixed Mn^{3+}–Mn^{4+} valency like in divalent or monovalent substituted materials and a magnetoresistive effect is consequently observed in these compounds. Manoharan et al. obtained a giant magnetoresistance $\Delta\rho/\rho_0 = 85\%$ at 210 K under 6 T in cubic $La_{0.7}MnO_{3-\delta}$ films grown by pulsed laser deposition on $LaAlO_3$ substrates [9]. More recently Gupta et al. have reported an interesting value of GMR at room temperature with $\Delta\rho/\rho_0 = 55\%$ at 300 K under 4 T in

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$La_{0.75}MnO_{3-\delta}$ films also grown by pulsed laser deposition on $SrTiO_3$ [10]. To our knowledge the chemical vapour deposition technique has never been used to synthesize such films.

2. Experiments

Films of composition $La_{1-x}MnO_{3-\delta}$ with various x values have been synthesized by using a new liquid source MOCVD process. The technological application of CVD requires the generation of highly stablilized vapour pressure of chemical compounds involving the elements which compose the layers; for some elements the precursors currently in use are thermally unstable and their volatility depends on the preparation procedure. The new process presented here [11] is based on the injection of micro-amounts of precursors dissolved in a convenient solvent. The volume injected is determined by the opening time of the injector (typically a few milliseconds) which ensures a very high reproducibility of the quantity of precursors injected and then of the vapour pressure. Several injectors can be simultaneously used for multilayers or for materials composed with two or three elements.

Fig. 1 presents the horizontal shaped reactor used for the deposition of our films. Tris (tetramethylheptanedionato) lanthanum and tris (tetramethylheptanedionato) manganese, $La(thd)_3$ and $Mn(thd)_3$, are used as precursors. They are dissolved in 1,2-dimethoxyethane as solvent and kept in a hermetically closed vessel pressurized under 1.5 bar of pure argon and connected to the injector.

Droplets of few microliters (typically 5 μl) are sequentially injected on a stainless steel porous belt lying on an oven which can be heated or not depending on the volatility of the solvent at the working pressure. The solvent which is immediately evaporated is in situ eliminated and the solid precursors deposited on the belt are mechanically transported into an evaporation zone (Fig. 1). The evaporated precursors are then carried by a mixture of O_2/Ar gases into a conventional hot-wall CVD reactor. Films growth was performed under the conditions given in Table 1.

3. Results and discussion

3.1. Composition and morphology of the films

$La_{1-x}MnO_{3-\delta}$ films of different compositions were grown simultaneously on MgO (100) and $LaAlO_3$ (102) single crystals. All the films are 0.5×0.5 cm^2

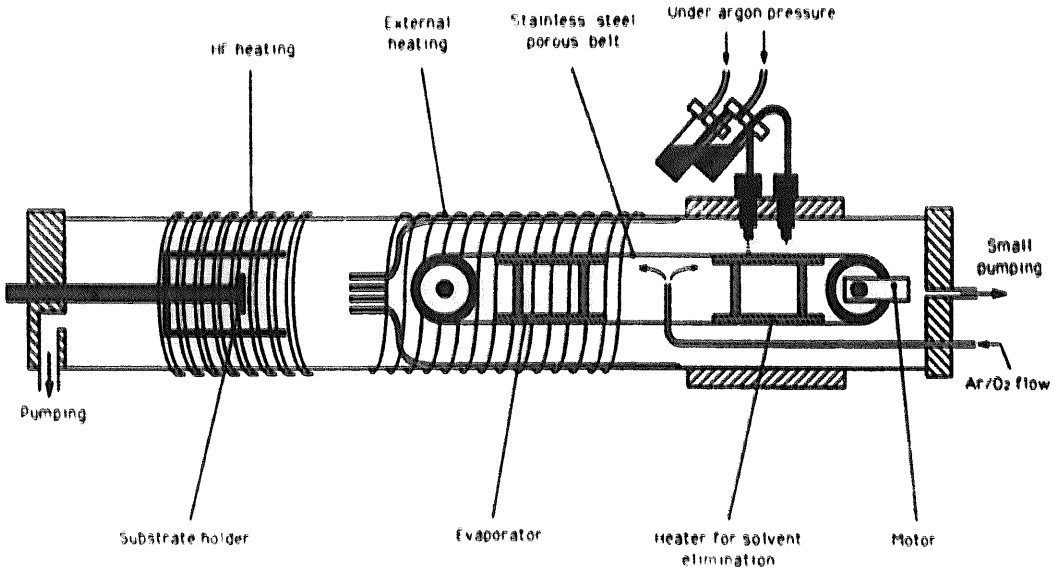

Fig. 1. Scheme of the reactor.

Table 1
Growth conditions of $La_{1-x}MnO_{3-\delta}$ films

Injection zone temperature	30°C	Number of injection	1600
Evaporator temperature	230°C	Volume of droplet	4.5 μl
Substrate temperature	650°C	Injection frequency	1 Hz
Total pressure	5.0 hPa	$La(thd)_3/Mn(thd)_3$ dilution	[0.93; 1.25]
O_2 flow	300 cm^3 min^{-1}		
Ar flow	300 cm^3 min^{-1}		

Table 2
Sources and films compositions

$(La/Mn)_{at}$ by WDS	$(La/Mn)_{at}$ by EDS	$(La/Mn)_{at}$ in the source
0.75	0.78	0.93
0.80	0.82	0.97
0.91	0.92	1.05
0.94	0.96	1.10
1.00	1.08	1.25

squares and exhibit a black mirror surface. The atomic ratio $(La/Mn)_{at}$ in the film was determined by wavelength dispersive spectrometry (WDS) and by energy dispersive spectrometry (EDS) but no direct measurement of oxygen has been carried out. Table 2 shows the relationship between the source and the film compositions.

We can note that the lanthanum content in the films is always smaller than that of the liquid source under the growth conditions we used. The La/Mn ratios given by WDS and EDS are very close. In the following we will consider the compositions given by the WDS to describe the films and Mn content will be normalized to 1 ($La_{0.75}MnO_{3-\delta}$, $La_{0.80}MnO_{3-\delta}$...).

The thickness which has been evaluated by cross-views on a scanning electron microscope is approximately the same for each film between 5300 and 5500 Å. Figs. 2a,b, respectively, show a cross-view and the surface of $La_{0.75}MnO_{3-\delta}$ on $LaAlO_3$.

3.2. Structural characterizations

Figs. 3a,b, respectively display X-ray diffraction patterns of $La_{0.91}MnO_{3-\delta}$ on MgO and $LaAlO_3$ in the $\theta/2\theta$ scanning mode ($\lambda_{Cu} = 1.54056$ Å). Only the (00ℓ) diffraction lines of the phase are present for films grown on $LaAlO_3$ substrates (200 000 counts for the 004 peak). Small (0$k\ell$) peaks are also observed for films grown on MgO (150 000 counts for the 004 peak) which evidences two kinds of textured LMO crystallites on this substrate.

This indicates a highly oriented film with the *c*-axis perpendicular to the plane of the substrate which is observed for each value of *x*. A more complete study using a four-circles diffractometer reveals that the crystal symmetry is cubic with a lattice constant $a = 2a_0$ where a_0 is the unit-cell constant of the basic perovskite structure: this may be due to a tilt of the oxygen octahedra in the structure whose study is in

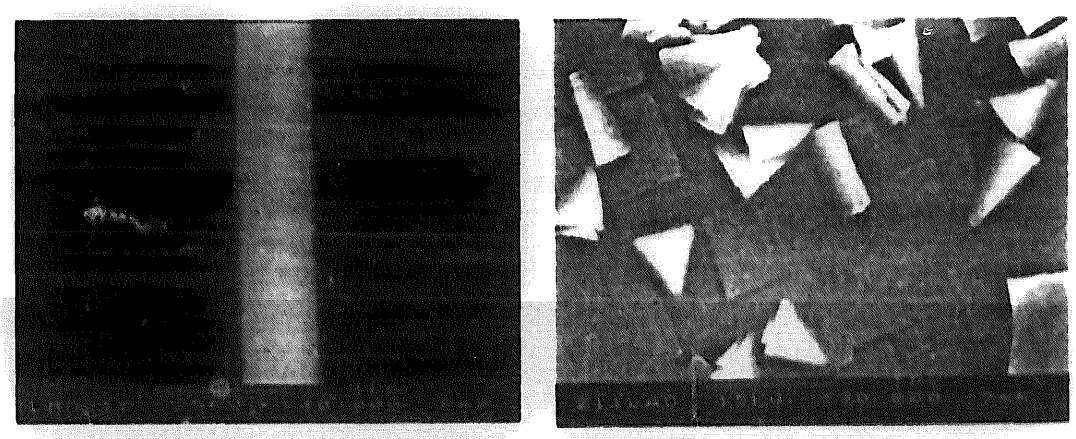

Fig. 2. (a) Cross-view of $La_{0.75}MnO_{3-\delta}$; (b) surface of $La_{0.75}MnO_{3-\delta}$ on $LaAlO_3$.

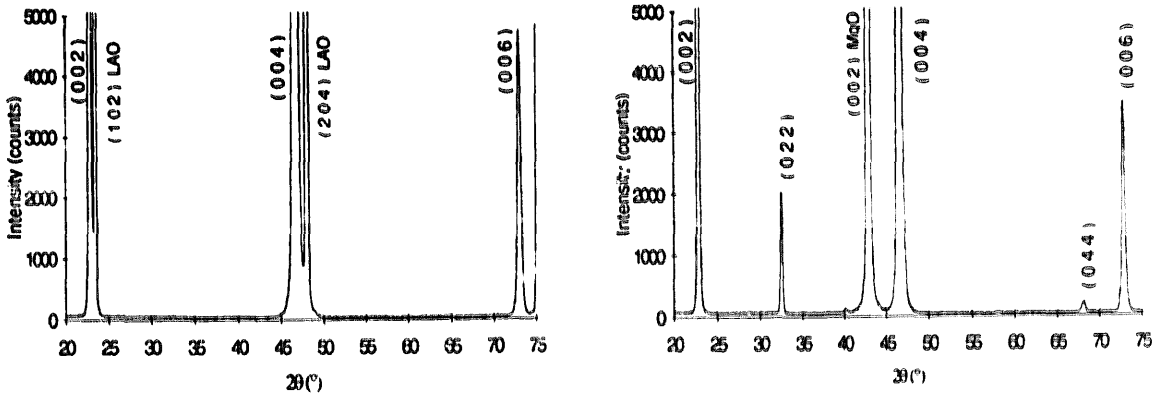

Fig. 3. X-ray spectra of $La_{0.91}MnO_{3-\delta}$ on $LaAlO_3$ and MgO.

Table 3
Variation of the cell parameter with x in $La_{1-x}MnO_{3-\delta}$ films

x value	Cubic parameter a
0	7.796(2)
0.06	7.792(2)
0.09	7.766(2)
0.20	7.756(2)
0.25	7.750(2)

progress. The rocking curves on the (004) peak of $La_{0.91}MnO_{3-\delta}$ have a full width at half maximum (FWHM) of 0.71° for films on $LaAlO_3$ and 1.59° on MgO. We observe on the different $\theta/2\theta$ patterns a small but constant variation of the positions of the LMO diffraction lines with x so that the lattice constant of the LMO phase decreases with increasing x as shown in Table 3.

A texture diffractometer was used in order to determine the epitaxial relationships between the LMO phase and the two kinds of substrates. Fig. 4a displays φ-scans performed on the (011) diffraction lines on LMO and MgO for $\chi = 45°$: the alignment of the poles leads to the following epitaxy: $\langle 100\rangle_{LMO}$ $//\langle 100\rangle_{MgO}$ and $\langle 010\rangle_{LMO}//\langle 010\rangle_{MgO}$. The same measurements achieved on films deposited on $LaAlO_3$ [poles (011) of LMO and (110) of $LaAlO_3$] also reveal an epitaxy with $\langle 100\rangle_{LMO}//\langle 100\rangle_{LaAlO_3}$ and $\langle 010\rangle_{LMO}//\langle 02\bar{1}\rangle_{LaAlO_3}$ (Fig. 4b). The FWHM of the peaks of the φ-scans are, respectively, 1.3° and 2.5° for $La_{0.91}MnO_{3-\delta}$ on $LaAlO_3$ and MgO.

The lattice mismatch between $La_{0.91}MnO_{3-\delta}$ and $LaAlO_3$ is only 2.5% against 7.6% for MgO. From these structural studies we can conclude that the epitaxy of $La_{1-x}MnO_{3-\delta}$ is better on $LaAlO_3$ than on MgO where a secondary orientation is observed and the FWHM of the different diffraction lines are two times broader.

3.3. Magnetic and electrical behaviour

Fig. 5 displays the temperature dependence of the magnetization for different samples. These measurements have been performed with a vibrating sample magnetometer under a constant field of 0.2 T. The transition temperature is found to increase as x increases i.e. as the Mn^{4+} content becomes larger (Table 4). We can notice a small shift of the magnetization for the film $x = 0.20$ around 160 K: this can be interpreted as a ferromagnetic-spin canting transition. The thickness and the area of the different samples were the same so that we can compare the different magnetic moments measured and state that they increase with x in relation to the ferromagnetic ordering when the Mn^{4+} content increases.

The electric resistance vs. the temperature at zero-field has been measured by using a four probe method for samples deposited on $LaAlO_3$ with $x = 0$, 0.09 and 0.25 (Fig. 6). Samples with low x values ($x = 0$ and 0.09) exhibit only a semiconductive behaviour which can be fitted very well by the Arrhenius formula $\rho = \rho_0 \cdot \exp(E_A/2\ kT)$ as shown on Fig. 6b; the activation energy is 0.26 eV for both samples. For the sample with the most important Mn^{4+} content ($x = 0.25$) a transition is observed at $T_p = 200$ K with a positive $d\rho/dT$ below T_p ($E_A = 0.24$ eV in the semiconducting region above T_p) but the behaviour remains semi-conductive below 140 K with a smaller activation energy ($E_A = 0.04$ eV).

Magnetoresistance measurements of the most lacunar film $La_{0.75}MnO_{3-\delta}$ were then measured. The temperature were varied in the range of 20–300 K; the field was applied parallel to the substrate and to the current up to 5 T. Figs. 7a,b, respectively show the resistivity and the GMR vs. the temperature and the field. The GMR was calculated using $\Delta\rho/\rho_0 = (\rho_0 - \rho_H)/\rho_0$ which is limited to 100%. We obtain a maxi-

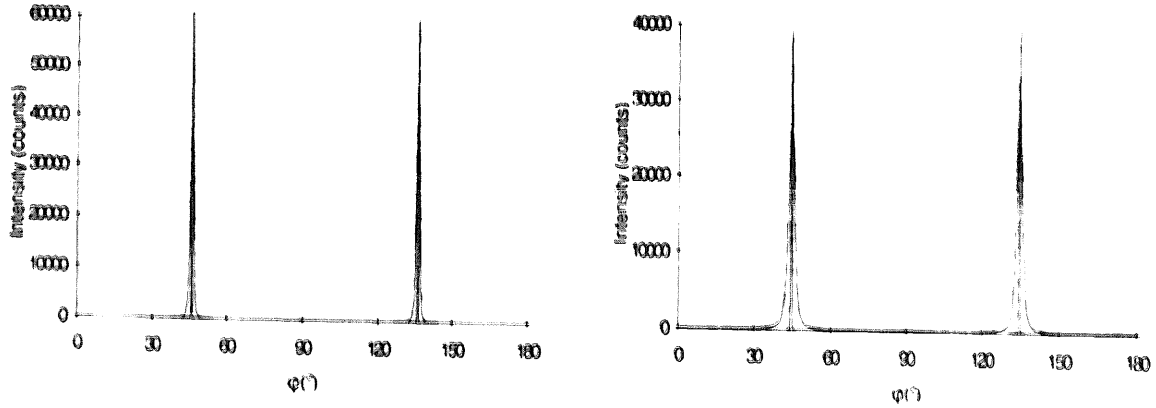

Fig. 4. (a) φ-scan on $(110)_{LaAlO_3}$ and $(011)_{LMO}$; (b) φ-scan on $(011)_{MgO}$ and $(011)_{LMO}$.

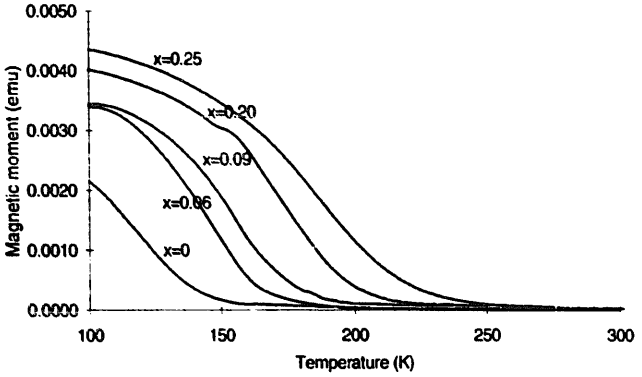

Fig. 5. Magnetic moment vs. temperature in $La_{1-x}MnO_{3-\delta}$ films.

Table 4
Variation of the magnetic transition temperature in $La_{1-x}MnO_{3-\delta}$ films

x value	T_c (K)
0	145
0.06	168
0.09	182
0.20	202
0.25	220

mum magnetoresistance of 75% under 5 T. The temperature of the peak of GMR is 190 K near the electrical transition temperature of 200 K. We can note that the variation of the GMR is linear in the [0 T; 2 T] range with a sensitivity of 25% per tesla.

The transition temperatures we get are quite far from those usually described for films doped with calcium or strontium or from Gupta's $La_{0.75}MnO_{3-\delta}$ films with a Mn^{4+} content similar to that expected in our films. In fact the oxygen stoichiometry of the films is probably deficient because of the low oxygen vapour pressure during the synthesis so that the Mn^{4+}/Mn^{3+} ratio is lower than that which we would get if the formula were exactly $La_{1-x}MnO_3$. Therefore various annealing experiments in air were carried out on $La_{0.80}MnO_{3-\delta}$ to study the influence of the oxygen stoichiometry on the physical properties. We obtain very interesting results which will be described elsewhere: a great improvement of the GMR properties is observed as it comes maximum at room temperature (300 K).

4. Conclusion

In summary, thin films with various lanthanum deficiencies $La_{1-x}MnO_{3-\delta}$ have been synthesized by using a new liquid source MOCVD technique on MgO (100) and $LaAlO_3$ (012) substrates. We get

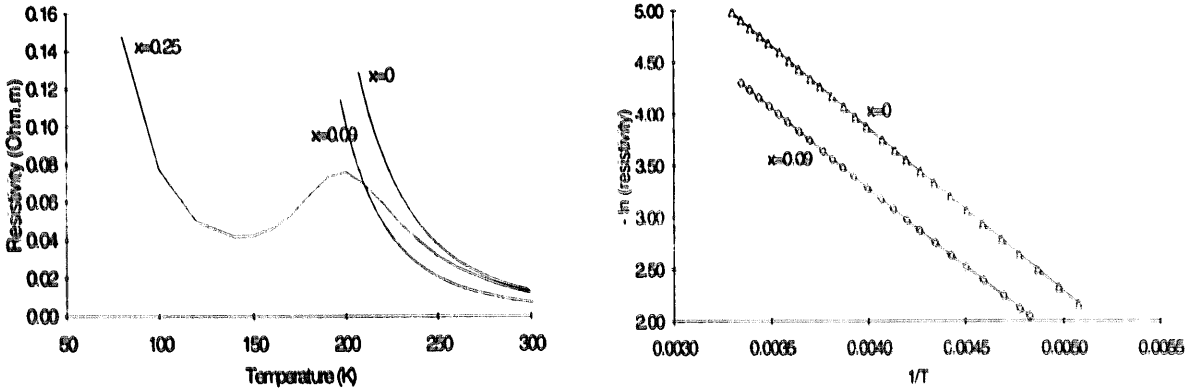

Fig. 6. Electrical behaviour vs. the temperature in $La_{1-x}MnO_{3-\delta}$ films for $x = 0, 0.09, 0.25$.

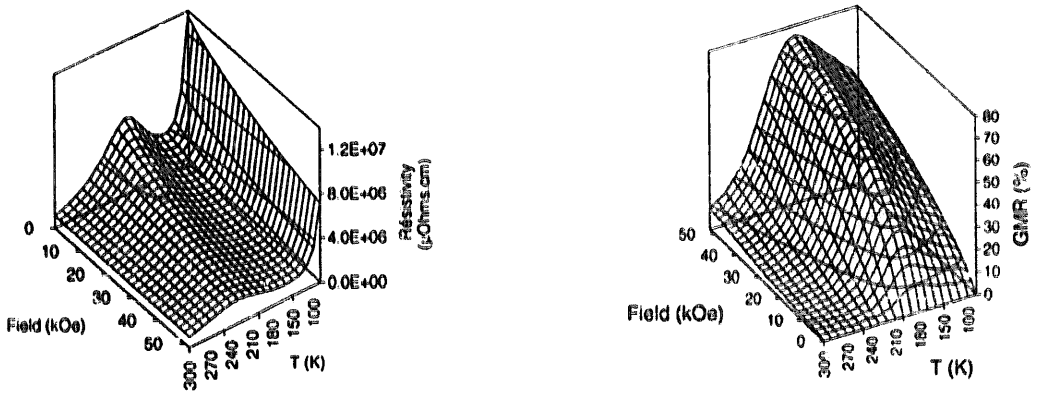

Fig. 7. (a) Resistivity vs. T and H; (b) GMR vs. T and H.

epitaxial films on both substrates with a better quality on $LaAlO_3$ (no secondary orientation). The T_cs of the as-deposited films are observed to increase with increasing x and are similar for the two kinds of substrate. Semi-conducting behaviour is observed for low x values. For the most lacunar film $La_{0.75}MnO_{3-\delta}$ an electrical transition is observed at 200 K very close to the T_c. A maximum magnetoresistive effect is then obtained at T = 190 K with a linear MR ratio of 25%/T in the [0 T; 2 T] range.

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