Chapitre 3:

Effet des joints de grain dans $La_{2/3}Ca_{1/3}MnO_3$

3 Effet des joints de grain dans $La_{2/3}Ca_{1/3}MnO_3$

Cette étude sur l'effet des joints de grain dans des couches de $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) a été motivée par la découverte de valeurs importantes de magnétorésistance à bas champs et directement reliées à la taille des grains dans les poudres de manganites, rapportée par Gupta [79] et Hwang [71]. Ces premières expériences montraient pour la première fois une magnetoresistance à bas champ (Low Field Magnétorésistance: LFMR) sur des couches de $La_{2/3}Sr_{1/3}MnO_3$ déposées sur des substrats polycristallins de $SrTiO_3$. Ces expériences et la rapide diminution de la magnétorésistance tunnel (TMR) avec la température dans des jonctions tunnel à base de manganites [73] ont mis en évidence l'importance d'études approfondies sur le transport dépendant du spin à travers les interfaces des manganites. La compréhension de l'effet des interfaces dans le transport est nécessaire avant d'utiliser les manganites comme la base de dispositifs utilisant leur caractère demi-métallique .

Le système modèle que nous avons développé dans ce chapitre est basé sur des couches minces de $La_{2/3}Ca_{1/3}MnO_3$ avec des joints de grains. Le but de ce travail est d'avoir une meilleure compréhension de l'effet des interfaces et des joints de grains dans les manganites.

Ayant comme objectif d'obtenir des films granulaires, nous avons réalisé une étude sur la croissance des couches minces de $La_{2/3}Ca_{1/3}MnO_3$ sur des substrats non accordés en paramètre cristallin de MgO(001) par ablation laser. Ces substrats ont été choisis parce qu'ils ont un large désaccord de maille avec LCMO (environ -9%) comme expliqué dans la section 3.1. Dans cette étude, nous avons contrôlé la texture des couches à partir de la température de dépôt. L'intérêt d'obtenir des couches granulaires avec cette méthode est qu'elle permet un meilleur contrôle des interfaces que dans des systèmes à base de poudres. En outre nous allons montrer que la température de dépôt est le paramètre permettant de faire apparaître ou non cette MR à bas champ.

Nous avons interprété la LFMR à partir des résultats de transport tunnel des spins à travers les joints de grains non complètement ferromagnétiques (FM). La pertinence de notre interprétation a été renforcée par la conception de différents systèmes granulaires qui nous ont permis de vérifier nos idées.

Nous avons étudié les différents phénomènes associés à l'existence de joints de grains dans les couches de $La_{2/3}Ca_{1/3}MnO_3$ comme par exemple la MR à fort champ (section 3.2.1), la LFMR (section 3.2.3) et la localisation à basses températures (section 3.2.3.2).

Notre modèle permet de discuter les différentes études rapportées sur des couches déposées sur des substrats bicristallins et sur des échantillons polycristallins [80-90] [91].

3 Effect of Grain boundaries in $La_{2/3}Ca_{1/3}MnO_3$

The present study on the effect of grain boundaries in $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) films was motivated by the discovery of large low field magnetoresistance and size dependent effects on granular manganites, first reported by Gupta [79] and Hwang [71]. These first experiments showed by the first time Low Field Magnetoresistance (LFMR) on $La_{2/3}Sr_{1/3}MnO_3$ films grown on polycrystalline $SrTiO_3$ substrates. These experiments and the rapid drop of TMR with temperature in manganite based tunnel junctions [73] evidenced the importance of further studies on spin transport through the interfaces of manganites. The understanding of the effect of interfaces in the transport is a necessary step prior the design of manganite based structure like tunnel junctions which uses the half-metallicity character of LCMO.

The model system we have developed in this chapter is based on $La_{2/3}Ca_{1/3}MnO_3$ thin films with grain boundaries. The aim of this work is to get deeper insight into the understanding of the effect of interfaces and grain boundaries in manganites.

In order to obtain granular films we have performed a study on the growth of $La_{2/3}Ca_{1/3}MnO_3$ films on non-matched MgO(001) substrates by pulsed laser deposition. This substrate has been chosen because its large mismatch (around -9%) with $La_{2/3}Ca_{1/3}MnO_3$ as is shown in section 3.1. In this study, we controlled texture by tuning the substrate temperature. The main interest of growing polycrystalline films is that it permits to have better control of the interfaces than in powder samples.

We have interpreted the LFMR effects based on spin tunneling through weakly FM Grain boundaries. The relevance of our interpretation was strengthened by designing different granular systems and checking our ideas.

We have studied the different phenomena associated to the existence of grain boundaries in $La_{2/3}Ca_{1/3}MnO_3$ films as the high field MR (section 3.2.1), the LFMR (section 3.2.3) and the low temperature localisation (section 3.2.3.2).

Our model systems allow us to discuss of different studies reported [80-90] [91] on films deposited on bicrystalline substrates and on polycrystalline samples.

In the following section, we present the study on the microstructure of $La_{2/3}Ca_{1/3}MnO_3$ thin film grown on non matched MgO (001) as a function of the substrate temperature during the thin film growth.

3.1 Manganite thin film growth

We have grown 60nm thick films of $La_{2/3}Ca_{1/3}MnO_3$ by the pulsed laser ablation technique using the third harmonic (355nm) of a Nd-YAG laser with a repetition rate of 10Hz (P=240mJ/pulse). The experimental set-up developed for pulsed laser deposition (PLD) of oxides is described in Appendix A:. Strain free films have been grown on non-perovskite substrates as MgO and epitaxial films on perovskite substrate $SrTiO_3$

In this section, a brief introduction to the different substrates used in this chapter and chapter 4 is presented.

3.1.1 Substrates

Perovskites have been grown on different kind of substrates and buffers by a large diversity of deposition techniques (PLD, sputtering, MBE, CVD, ..). The choice of the substrate is the key parameter to determine the film properties .

The most commonly used substrates to grow mixed valence manganites are MgO, $SrTiO_3$, $LaAlO_3$, $NdGaO_3$ and Si. Direct growth on Si substrates is a technological challenge due to the fact that as manganite deposition is done at high substrate temperature, chemical reaction with substrate happens, and in an oxidising atmosphere the growth is done on polycrystalline SiO_x giving rise to polycrystalline films. Textured growth on Si can be achieved using buffer layers [92, 93]. In Tab. 3-I are shown the crystallographic characteristic of these substrates and in Fig. 3-1 is sketched their crystallographic structure.

The cell parameter of the pseudocubic perovskite structure of $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) is 3.85Å. From the lattice mismatch point of view, $NdGaO_3$ (-0.2%), $SrTiO_3$ (-1.3%) or $LaAlO_3$ (1.7%) are the most convenient substrates for LCMO epitaxial growth. Nevertheless $LaAlO_3$ has the disadvantage of being twinned due to a crystallographic distortion of the perovskite structure taking place at 510°C. Hence, $SrTiO_3$ (STO) or $NdGaO_3$ seemed to be the best candidates for epitaxial film growth due to the large lattice mismatch (≈-9%) of MgO.

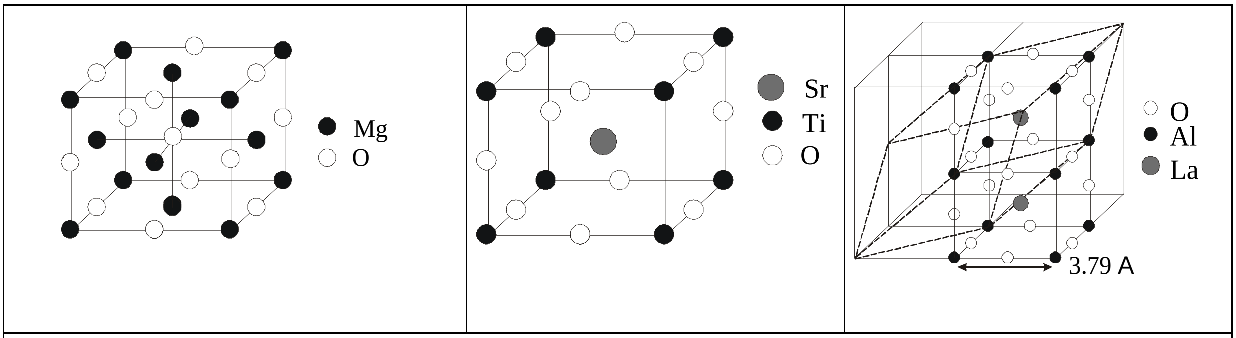


Fig. 3-1 *Different crystallographic structures for MgO, $SrTiO_3$ and $LaAlO_3$*

Two systems have been extensively studied in the present work: films of LCMO on MgO (001) and on STO (001) (chapter 4).

Tab. 3-I *Crystallographic description and thermal expansion coefficient of the most commonly used substrates for manganite film epitaxial growth*

Substrate	Crystallographic structure	Cell Parameters (Å) at 300K	Thermal expansion coef ($10^{-6}K^{-1}$)
MgO	cubic (NaCl)	a_c=4.216	12.8
$SrTiO_3$	Cubic (perovskite)	a_p=3.905	10.30
$NdGaO_3$	Tetragonal	a=b=3.863 ; c=3.854	11
$LaAlO_3$	Rhombohedric	a_R=3.79	9.20

In the following section, we describe the dependence of LCMO films microstructure deposited on MgO substrates on the substrate temperature during the deposition.

3.1.2 Textured and non-textured growth of $La_{2/3}Ca_{1/3}MnO_3$ on MgO(001)

The substrate temperature during deposition is one of the parameters determining the microstructure of the films. Different growth modes can be distinguished according to substrate temperature:

a) Low temperature: it favours the formation of polycrystalline films with small grains because the atoms arriving at the surface of the substrate do not have enough energy to join the lowest energy equilibrium positions. A polycrystalline microstructure is developed due to the existence many nucleation centres that do not have crystallographic coherence between them.

b) High temperature: it favours the formation of polycrystalline films with large volume diffusion, recrystallisation and large grain formation.

Slightly above the optimum substrate temperature for layer by layer growth, the surface diffusion dominates the crystal growth and the microstructure obtained consists in grains with columnar shape and height that can reach the film thickness.

Several growth parameters were optimised to obtain the highest quality thin films. In this sense, manganite film deposition was carried out under 300mTor of oxygen pressure and cooling down at 5°/min in 1 bar of O_2 needed to guarantee the good oxygen stoichiometry. Other growth parameters are described and analysed in Appendix A:.

We have performed a study on the film microstructure as a function of the substrate temperature that allowed us to determine the temperature range for “epitaxial” growth of LCMO on MgO. We recall that strictly speaking, epitaxy means texture in the three crystallographic directions and full crystallographic coherence (ex. same crystal structure for film and substrate). In the following, we will treat LCMO as a cubic crystal and we will call epitaxial films those which present three-axis-texture.

Epitaxial films:

In LCMO films on MgO(001) the temperature range for epitaxial growth has been found to be 670°C<$T_{substrate}$<780°C.

In the θ-2θ patterns only the (00●) reflections appear and no trace of other reflections from perovskite structure are observed (Fig. 3-2). The additional series of Bragg peaks observed correspond to the single crystal MgO substrate and to the sample holder and are identified in Fig. 3-3.

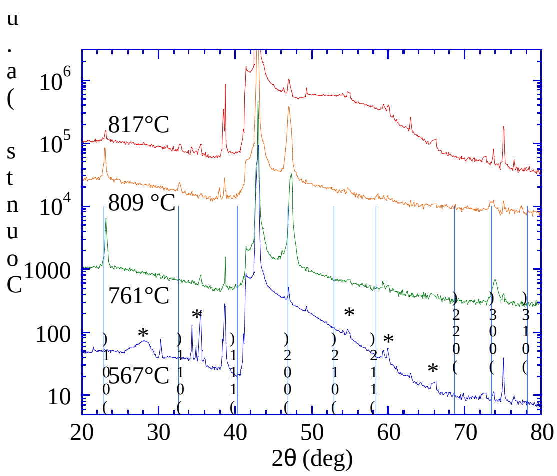


Fig. 3-2 *X-Ray θ-2θ diffraction patterns of LCMO films on MgO (001) substrate for different deposition temperature. Peaks marked with * are identified to be from the diffractometer sample holder*

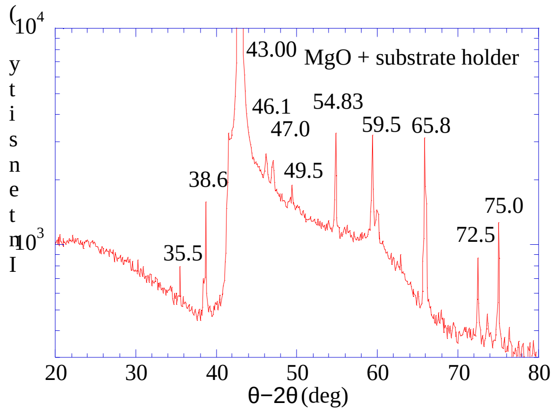


Fig. 3-3 *X-Rays θ-2θ diffraction pattern of a clean MgO (001) substrate on a sample holder*

Using the Laue-Scherrer formula for the (002) LCMO peak, we have checked the size of the crystallites that give intensity to the (002) reflection. The Laue-Scherrer formula (Eq. 3-1) gives an estimation of the mean particle diameter *t* in powder diffraction patterns from the measured angular half width at half maximum ε^* $=\Delta 2\theta/2=\Delta\theta$ and the peak position (2θ). Sometimes an additional prefactor (0.9) is used. The instrumental incident beam aperture ε_0 also contribute to the peak broadening, so ε^* is the difference between the experimental angular half width and the instrumental beam aperture ε_0 (ε_0 ≈0.19°).

$$t = \frac{\lambda}{\varepsilon^{*} \cos\left(\frac{2\theta}{2}\right)} \qquad \textbf{Eq. 3-1}$$

The result obtained for the (002) peak of LCMO epitaxial film (Fig. 3-4) is a coherent film thickness of 50nm which is about 16% less than the film thickness measured by optical reflectivity performed during the film growth (60 nm).

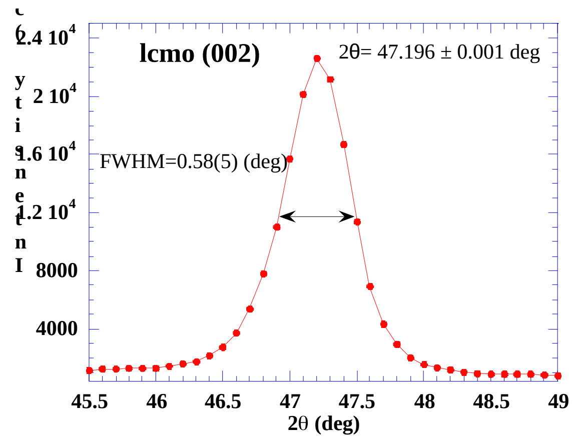


Fig. 3-4 *XRD θ-2θ measurements around the (002) peak of a 60nm thick epitaxial LCMO film on MgO(001)*

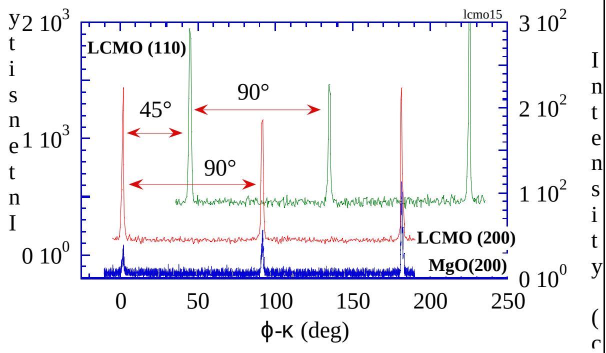


Fig. 3-5 *X-Rays GID measurements on a epitaxial 60nm thick LCMO film on MgO (001)*

The grazing incidence X-Rays diffraction (GID) on textured films allowed us to check the epitaxy relations as well as to determine the in plane cell parameter. The epitaxy relations correspond to LCMO (200)½½MgO(200). There are no other peaks than the cubic symmetry peaks that appear every 90° in a ϕ scan (Fig. 3-5). On the other hand, the (110) reflection of LCMO is at 45° from the (100) of MgO as expected from the epitaxy relation.

The determination of the in-plane lattice parameters has been done through a small step scan in the GID using correlated ϕ and 2χ movement (Fig. 3-6). The cell parameter values obtained agree with the existence of a cell parameter modification compared to the LCMO bulk value. However, the 9% lattice mismatch between MgO and LCMO indicates that it is energetically impossible for the film to completely expand in the in-plane direction to reach the MgO in-plane lattice parameter.

The in-plane grain size has also been estimated to be between 60nm to 180nm in the epitaxial growth region.

Rocking curves on the epitaxial films of LCMO on MgO have been performed in order to know the crystallographic misalignment between crystallites. The rocking curve of the (110) in-plane peak gives 1.5° of crystallite misalignment for a 60nm thick epitaxial film of LCMO on MgO (Fig.

3-7). Such value for the rocking curve is not too large for the *ab* plane if we take into account the 9% of lattice mismatch between LCMO and MgO.

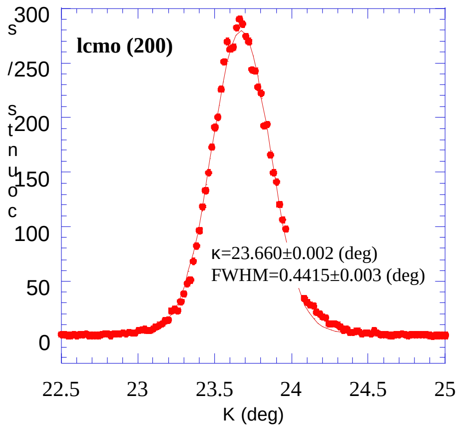


Fig. 3-6 *GID measurements around the (200) peak*

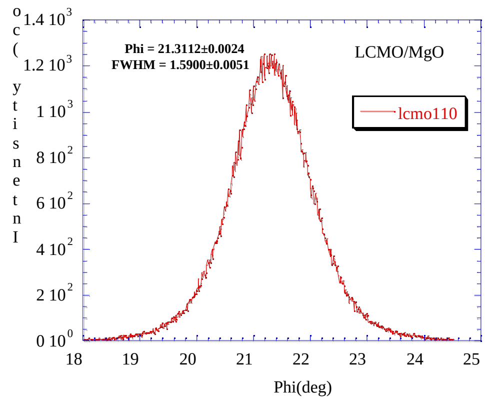
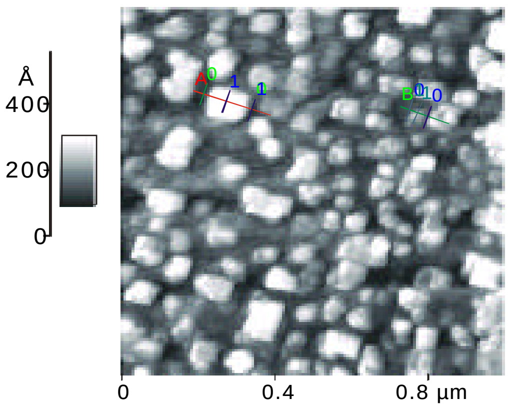


Fig. 3-7 *X-Rays in plane rocking curve around the (110) peak of a 60nm LCMO film on MgO (001)*

In addition, Atomic Force Microscope (AFM) measurements in contact mode on LCMO epitaxial film on MgO ($T_{substrate}$= 760°C) permit to observe the existence of grains. The grains have a squared shape and can be distinguished from droplets (Fig. 3-8). There exists a distribution of grain sizes ranging between 0.1µm to 0.05 µm in the selected area in agreement with GID measurements.

The height of the observed structures is variable. In Fig. 3-8 the grains height is about 10-20nm and taking into account the film thickness of 60nm means that nearly 1/3 of the thickness is constituted by columnar type grains not connected in the plane direction.



Line	Height	Distance	Angle
[A]	0: 14.5 Å 1: 233 Å	0: 0.136 um 1: 744 Å	0: 0.6° 1: 17.4°
[B]	0: 25.1 Å 1: 106 Å	0: 496 Å 1: 211 Å	0: 2.9° 1: 26.6°

Fig. 3-8 *AFM measurements on 1µm² of the LCMO film deposited on MgO at 760°C*

A GID study of LCMO films on MgO has been performed as a function of the substrate temperature on a series of 60nm thick LCMO films on MgO. The ϕ-2χ scans around the (200) reflection of LCMO are shown as a function of the deposition temperature (Fig. 3-9). The study shows that the reflection is narrower as higher is the deposition temperature. It agrees with the fact that for higher substrate temperatures the crystallites are larger.

Polycrystalline films:

For substrate deposition temperatures below the epitaxial temperature range, there exists a zone of polycrystalline 3D films (Fig. 3-2 T=567°C). Too high substrate temperatures (T>780°C) also induce 3D polycrystalline growth as can be deduced from the loss of intensity of the perovskite Bragg peaks (Fig. 3-2 T=817°C).

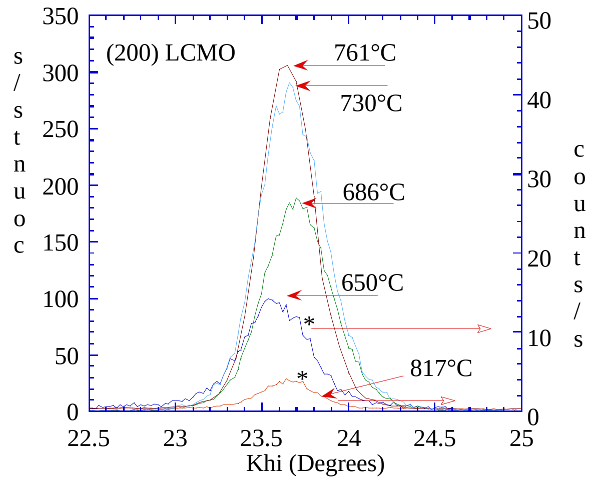


Fig. 3-9 *(200) reflection of LCMO on MgO as a function of the deposition temperature*

For deposition temperatures slightly below the range for epitaxial growth there is a temperature range where bitexture is observed. The X-Ray θ-2θ pattern showed the existence of the (001) and (110) reflections indicating the existence of a certain number of grains with these crystallographic directions out of the film plane. In addition, grazing incidence patterns around the (110) reflection appeared every 45° instead of 90°(Fig. 3-10) while the (200) reflection was found every 90°. These measurements suggested that the film consisted in a double population of textured grains (Fig. 3-11) following the epitaxial relations: LCMO (001)½½MgO(001) and LCMO (110)½½MgO(001).

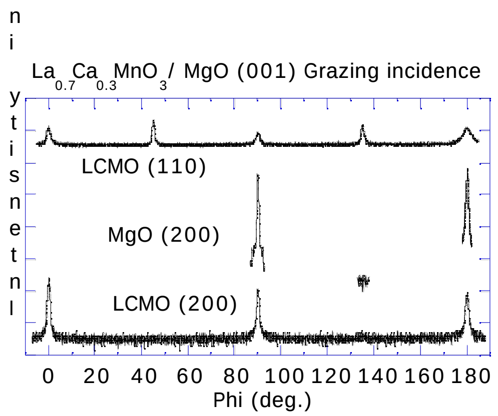


Fig. 3-10 *X-Rays grazing incidence measurements of the LCMO film on MgO (001) displaying a double texture*

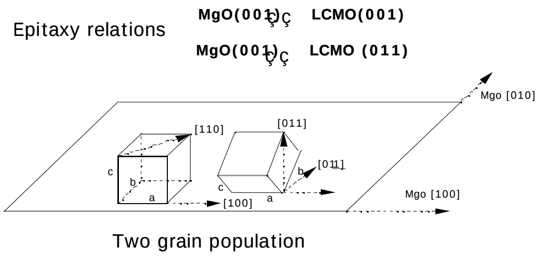


Fig. 3-11 *Schematic representation of the crystallographic double texture displaying the orientation of the two types of grains*

Similar structural characterisations have been performed for films of substrate temperature in the range of our study 550°C <T<830°C.

The integrated intensity of the (200) peak (GID) increases with the substrate deposition temperature up to the optimum deposition temperature (≈760°C) (Fig. 3-9). The integrated intensity of the Bragg peak can be correlated to the number of grains diffracting in this direction and is an indication of the degree of polycrystallinity.

We have determined the in-plane and out-of-plane cell parameters of the different films by fitting with pseudo-Voigt function the (00●) peaks of the LCMO films. In order to reduce systematic errors we checked the position of the $\lambda_{k\beta}$ and $\lambda_{k\alpha}$ (002) peaks of MgO. However, the low intensity of the in-plane reflections for the polycrystalline peaks induces a large error on the cell parameters.

The evolution of the in-plane and out-of-plane lattice parameter of LCMO films on MgO (001) substrates with the deposition temperature (Fig. 3-12) shows discontinuous behaviour. Films deposited at low and high substrate temperatures ($T_{substrate}$<670°C or $T_{substrate}$>780°C) are polycrystalline, and their lattice parameter is closer to the bulk target lattice parameter.

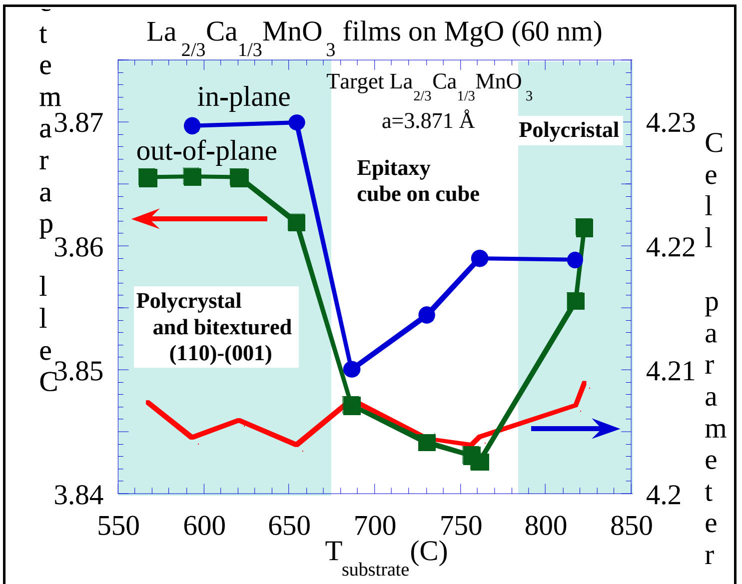


Fig. 3-12 *Diagram of the epitaxy regions and evolution of the out of plane cell parameter of LCMO films on MgO substrate as a function of the substrate temperature.*

Epitaxial films were found in the substrate temperature range between 670°C>$T_{substrate}$>780°C and showed smaller out-of-plane cell parameter than the polycrystalline film. For the optimum deposition conditions LCMO grows textured along three axis on MgO but do not have MgO cell parameters.

In conclusion, we have grown a series of 60nm thick films of LCMO on MgO (001) substrate at in the substrate temperature range of 550°C <T<830°C. This detailed study allow us to synthesise a polycrystalline model system:

a) The existence of a 100°C wide deposition temperature range for “epitaxial” growth (670°C<$T_{substrate}$<780°C).

b) All the films are crystallographically granular and grain size increases with deposition temperature. Grains become textured in the "epitaxy" range.

c) A tendency of grain size increase when increasing the deposition temperature of the films

d) The existence of distorted unit cell in epitaxial films while polycrystalline films cell parameters are similar to the bulk material

In the following section, we present the effects of the existence of grain boundaries on the magnetotransport measurements.

3.2 Magnetotransport and magnetism in granular films

Studies on magnetotransport properties have been performed on epitaxial and polycrystalline films in a temperature range between 1.5K-300K and with magnetic fields up to 30T.

The effect of grain boundaries on the magnetotransport properties has been studied in different systems in the present work and in all the systems the existence of grain boundaries are at the origin of many characteristic features.

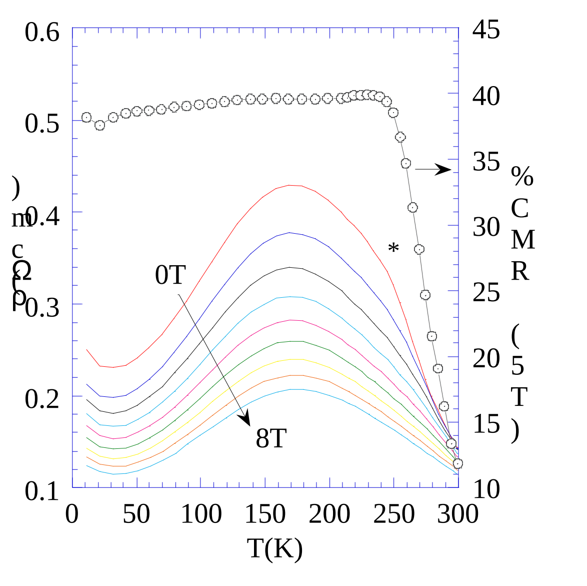


Fig. 3-13 *Thermal evolution of the resistivity under several applied magnetic fields and magnetoresistance under 5T of applied magnetic field of an polycrystalline 60nm LCMO film on MgO(001)*

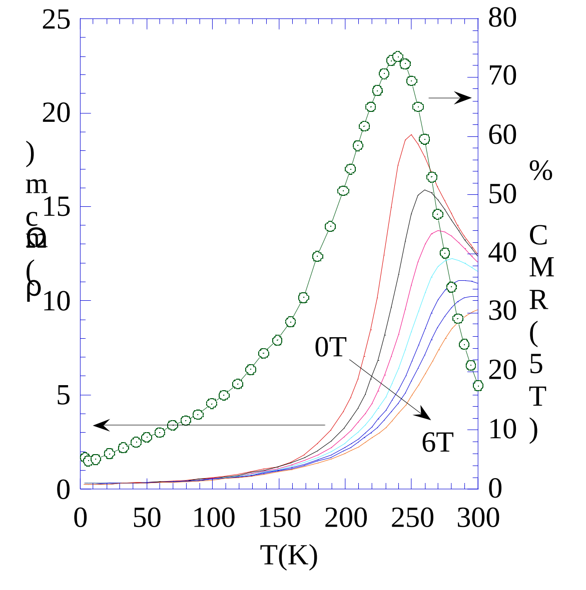


Fig. 3-14 *Thermal evolution of the resistivity under several applied magnetic fields and magnetoresistance under 5T of applied magnetic field of an epitaxial 60nm LCMO film on MgO(001)*

A comparison between magnetotransport behaviour of epitaxial (Fig. 3-13) and polycrystalline (Fig. 3-14) films of LCMO on MgO(001) reveal that polycrystalline films display:

i) Rather high value of the residual resistivity compared to that of a single crystal or epitaxial films (0.23Ωcm for polycrystalline films compared to the140µΩcm for LCMO single crystal or 300µΩcm for epitaxial films on MgO).

ii) A metal/ insulator transition temperature around fifty degrees below the Curie temperature (Fig. 3-15).

iii) A kink (* in Fig. 3-15) in the resistivity curve at the T_C of the film

iv) Development of localising effects at low temperatures which give rise to an upturn of the resistivity below 15K.

v) Lower MR: ≈40% to 50% of MR in 5T obtained at T_C (Fig. 3-13) which is lower than the values obtained in epitaxial films (around 80% Fig. 3-14)

vi) The CMR that remains rather constant upon cooling in contrast to epitaxial films where the CMR peaks at T_C .

vii) Large magnetoresistance under fields of the order of the coercive field (few mTesla).

All these effects present in polycrystalline films are an indication that several processes are contributing to the resistivity: intrinsic processes, reflected in the kink of the resistivity at T_C, and extrinsic processes that give rise to the upturn of the resistivity at low temperature and are responsible of the high value of the resistivity below the M-I transition as well as the temperature of the M-I transition.

The intrinsic contribution to the resistivity comes from the inside of the grains while the extrinsic contribution is due to the presence of grain boundaries. The fact that from the magnetic point of view there is no difference between the thermal evolution of the magnetisation of the polycrystalline film and epitaxial films is a proof that the inside of the grains contains the same LCMO phase than epitaxial films. In the following, we define T_C as the temperature of maximum slope of the magnetisation and we obtained T_C= 226.4K in epitaxial films which is around 40K below the bulk value.

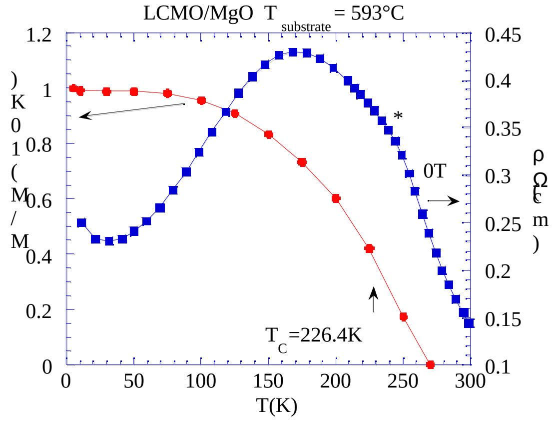


Fig. 3-15 *Thermal evolution of the normalised spontaneous magnetisation and resistivity characteristic of polycrystalline films.*

Several authors have claimed that grain boundaries could be zones of chemical segregation as it was stated in doped semiconductors [94]. If such chemical diffusion exists it should be dependent on the temperature of the substrate during deposition. But, the characteristic energy for the transport behaviour above the maximum of the resistivity, for polycrystalline films deposited at low and high temperatures, is very similar, so indicating that the grain boundaries are similar at high and low deposition temperature. In section 3.3, we will show that granular behaviour can be obtained in an artificial grain boundary made at RT and where cation diffusion does not occur.

Another possible hypothesis is the existence of electronic segregation. This effect could generate a large distribution of electronic and magnetic states at the surface of the grains ranging from insulating-FM to charge ordered-AF as pointed out from HREM images on thin LCMO films on $LaAlO_3$ [95] and can not be discarded.

The coercive field at 10K slightly decrease with the substrate temperature independently of the texture range (Fig. 3-16).

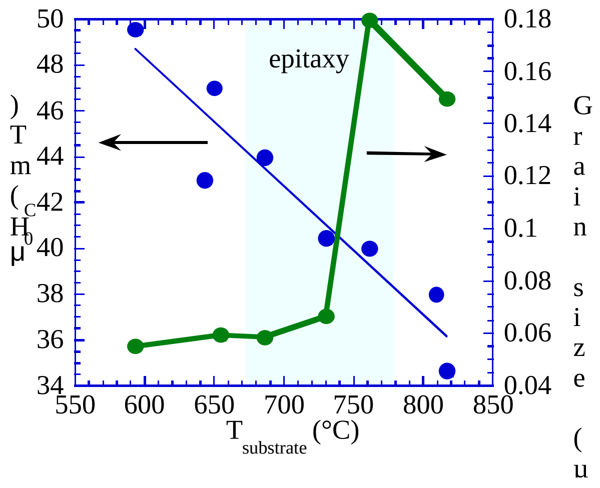


Fig. 3-16 *Comparison of the coercive field at 10K for polycrystalline and epitaxial LCMO films on MgO***.**

In conclusion, the existence of grain boundaries (GB) is reflected mainly in resistivity measurements while magnetisation measurements do not display much difference between polycrystalline and epitaxial LCMO films on MgO(001) substrate.

It should be noticed that in the previous section we found that epitaxial films of LCMO on MgO(001) substrate are also formed by grains and thus there exists a similar number of GB. However, these films do not display granular type magnetotransport behaviour.

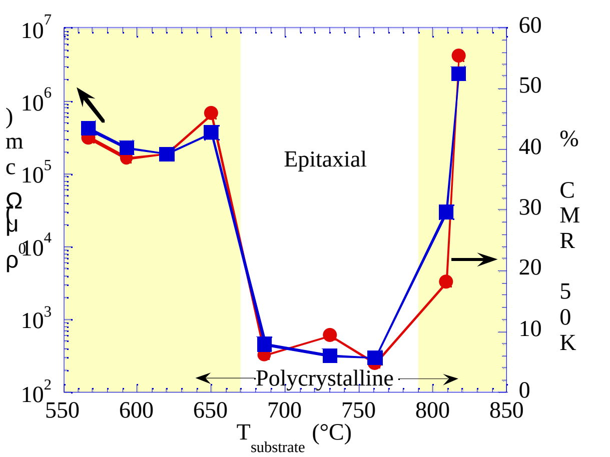


Fig. 3-17 *Residual resistivity and MR at 50K vs substrate temperature.*

There is a direct relationship between the residual resistivity of the films and their microstructural characteristics (Fig. 3-17). In metals, the residual resistivity is a measure of the defect or impurity concentration. In the manganite case, it is an indication of the density of badly connected grain boundaries (if one considers that the inside of the grains has the same residual resistivity than in a single crystal). The value of the MR observed at 50K is also displayed in Fig. 3-17. Its evolution is identical to the behaviour of the residual resistivity. MR at 50K appears for polycrystalline films, while it is strongly reduced in epitaxial films.

3.2.1 High Field Magnetoresistance ($T<T_C$)

Specific feature observed in polycrystalline films is the existence of a larger high field magnetoresistance compared to epitaxial films at temperatures below T_C.

The magnetoresistance at 10K for 60nm thick LCMO films on MgO (001) substrates and different substrate temperature corresponding to different microstructure is shown in Fig. 3-18. The high field slope at low temperatures changes with the microstructure of the film. Moreover, there is no universal high field slope for all the microstructures in the measured range of magnetic fields. This aspect differs from the opinion of some other authors [96] who conclude that the high magnetic field slope is independent of the microstructure of the polycrystalline films.

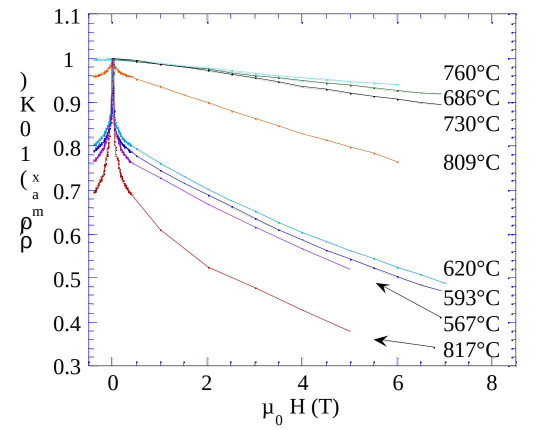


Fig. 3-18 *Magnetoresistance at 10K for LCMO films on MgO with different microstructure tuned by the substrate temperature during film growth.*

In general, granular films exhibit lower MR at T_C (MR≈40%) than epitaxial films (MR≈80%) but in granular films, MR is constant down to low temperatures in contrast with the epitaxial films which display highly reduced MR in the FM state (Fig. 3-19, Fig. 3-20).

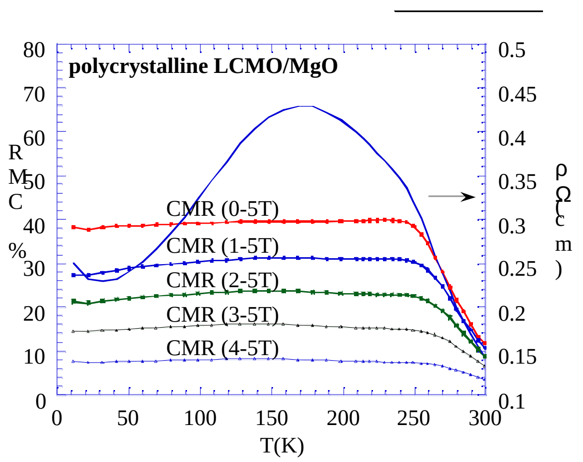


Fig. 3-19 *Evolution of the MR for different applied magnetic fields in polycrystalline films.*

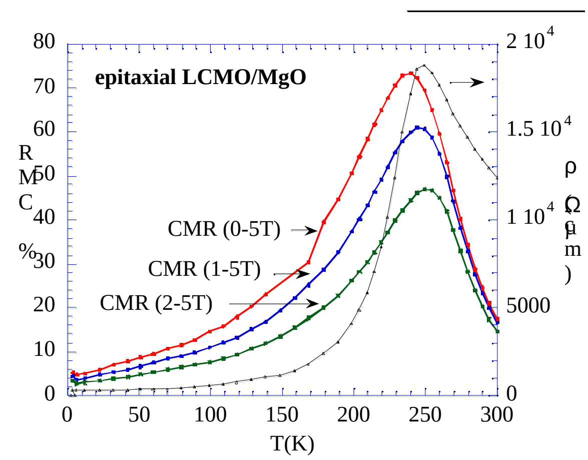


Fig. 3-20 *Evolution of the MR for different applied magnetic fields for epitaxial films.*

Fig. 3-21 summarises the tight relation between the MR at low temperature and at T_C and the microstructure as a function of the deposition temperature.

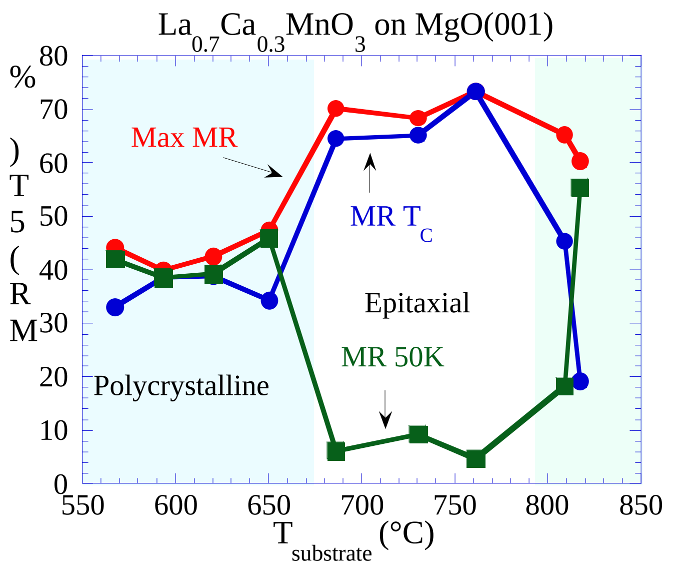


Fig. 3-21 *Evolution of the CMR (T_C) and at low temperature (50K) with the substrate temperature of LCMO films on MgO (001).*

In the following, we demonstrate that the application of large fields permits to nearly saturate the MR in epitaxial and polycrystalline films. For that reason, we have performed a series of magnetotransport measurements at the Service National de Champs Magnétiques Pulsés de Toulouse (SNCMP). Pulsed magnetic fields up to 30T were obtained after the discharge of a series of bank capacitors on a resistive coil giving rise to fields up to 30T in 100ms. The measurements were performed on the same LCMO films on MgO (001) presented above, using the four contacts technique in a dc current mode.

Measurements were taken when increasing and decreasing the magnetic field, however due to the characteristics of the field given by the resistive coils only the decreasing field measurement is taken into account due to artefacts produced in the increasing field measurement.

The resistive coils are immersed in a liquid nitrogen bath and a pulse of 10KV arrives to the coils thanks to an optically activated switch able to discharge a bank of several tens of capacitors at the same time. Once the maximum field is reached, the field decreases exponentially. The pulse lasts 1.7s taking into account the increase and decrease of the field.

The aim of this measurements is to analyse the magnetotransport behaviour of LCMO epitaxial and granular films on MgO(001) substrate in the magnetically saturated state.

We have chosen three types of characteristic films from the microstructural point of view (Fig. 3-22). The films were chosen to be representative of the three regions of growth: polycrystalline deposited at low temperature, epitaxial and polycrystalline deposited at high temperature.

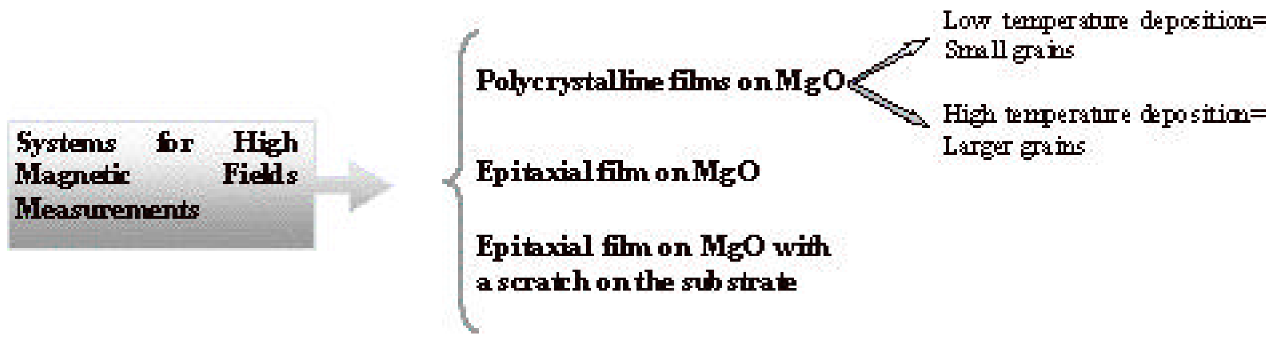


Fig. 3-22 *Schema of the films measured under high applied magnetic fields.*

An additional new system was used in high field magnetoresistance measurements. It consists in a epitaxial film grown on a scratched MgO substrate. In the next section, we present its microstructural characterisations.

3.2.1.1 Artificially created GB: scratched film

In order to produce a disordered region in an epitaxial film, on a clean MgO substrate three lines separated by 0.5mm had been performed with a diamond pencil. A 60nm thick LCMO film was deposited on this substrate using the same deposition conditions as the epitaxial film used in the high fields measurement. Therefore, the only difference between the epitaxial and the scratched films is the disorder at the artificial traces in the latter.

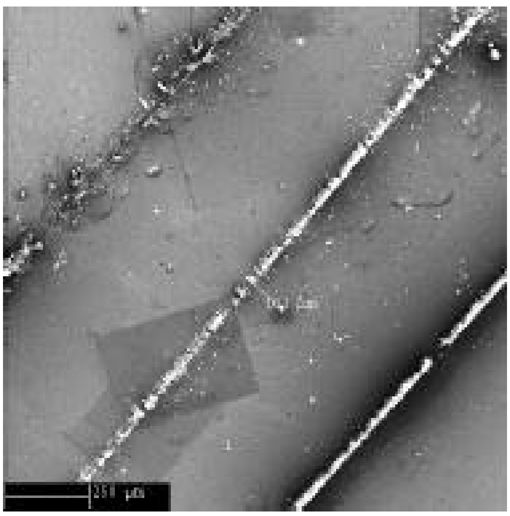


Fig. 3-23 *SEM image of the three traces on the scratched film of LCMO on MgO.*

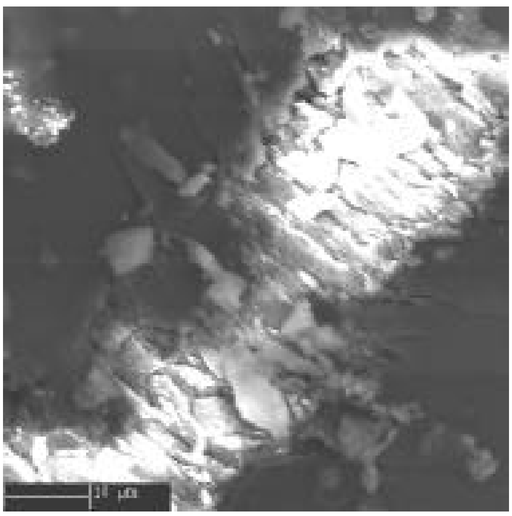


Fig. 3-24 ***SEM image of the scratched zone.***

The width of the traces is around 10.4µm from SEM images (Fig. 3-23, Fig. 3-24). SEM observations permit to verify that the film is continuous (that fact agrees with the metallic character through the scratch).

In our study the scratched film is also called epitaxial discontinuous film (ED) in order to distinguish it from the non-scratched epitaxial film.

Resistivity measurements performed through the scratched zone under applied magnetic fields up to 5T allows distinguishing the metal-insulator transition around 230K. The residual resistivity of the scratched film is two orders of magnitude larger than in the continuous film (34 mΩcm-scratched vs 461µΩ cm-continuous).

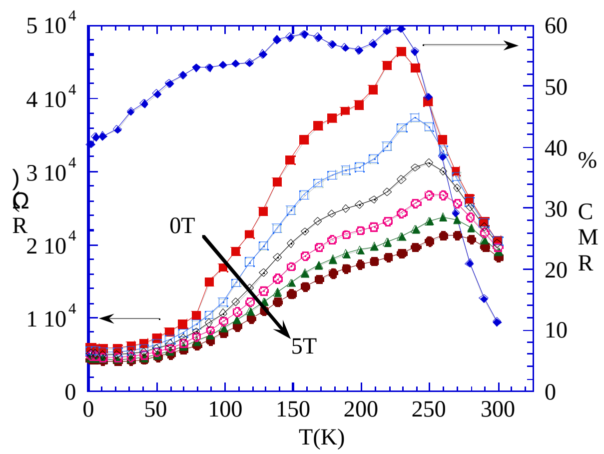


Fig. 3-25 *Magnetotransport measurements on the scratched LCMO film on MgO*

Ootther striking features are the existence of a second bump in the resistivity measurement around 170K and of considerable MR down to low temperature, which are characteristic of granular behaviour.

However, no evidence of low temperature localisation has been observed in this film. This is in the basis of the hypothesis that the low temperature localisation and the maximum of the resistance at temperatures around 150K do not have the same physical origin.

Granular behaviour of the scratched epitaxial film rules out the possibility of attributing the granular effects observed in polycrystalline films to the existence of a second manganite phase due to the low or high deposition temperature because the film deposition of the scratched substrate is carried out at the same temperature as the epitaxial film.

3.2.1.2 High Field magnetotransport on epitaxial continuous and discontinuous films

Magnetotransport measurements performed with fields up to 30T revealed the differences at high applied magnetic fields between the continuous (Fig. 3-26) and discontinuous film (Fig. 3-27):

a) At 4K the discontinuous film displays twice the MR of the continuous film.

b) Discontinuous film displays more curvature of the MR at low fields and do not seems to saturate up to higher magnetic fields.