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High-quality in situ manganite thin films by pulsed laser deposition at low background pressures

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Abstract. We show that by decreasing the laser fluence it is possible to improve the oxidation process in manganite thin films under low background oxygen pressure, allowing the in situ use of conventional Reflection High Energy Electron Diffraction diagnostic. Films deposited at low fluence (corresponding to a deposition rate per pulse lower than 10^{-2} unit cells per laser shot) show a two-dimensional growth mode and possess very good transport properties without the necessity of any further post-growth annealing treatment. A physical model, based on the plume-background interaction as a primary mechanism of film oxidation during growth, is proposed to explain the experimental findings.

PACS. 79.20.Ds Laser-beam impact phenomena – 81.15.Fg Laser deposition – 75.70.-i Magnetic properties of thin films, surfaces, and interfaces

1 Introduction

Nowadays, several techniques, as sputtering [1], molecular beam epitaxy (MBE) [2] and pulsed laser deposition (PLD) [3] are routinely used to prepare high quality thin films of manganites. One advantage of the PLD technique is that high deposition rates can be achieved by simply increasing the laser repetition rate. This approach has been exploited to impose a "two-dimensional" growth mode in perovskite systems by the so-called "interval deposition" method. This method consists of depositing one unit cell layer thick in a very short time, this is followed by a much longer pause during which the material can crystallise [4], though precisely in this high-deposition rate regime it is often difficult to fully oxidise each layer during deposition [5]. Optimisation of the magneto-transport properties of manganite films depends strongly on achieving the correct oxygen stoichiometry. More importantly for the fabrication of multilayer oxide heterostructures it is often crucial that each layer is correctly oxidised *during* deposition. Two different mechanisms for film oxidation can be envisaged: either direct vapour oxidation during deposition or oxygen diffusion through the surface into the film after deposition. The former mechanism is activated by a background of oxidizing gas and depends on the gas pressure, the latter by post-deposition oxidizing and annealing treatments. Oxidizing gases, such as O_2 [6], N_2O [7] and ozone [8] have been used. The difference in the minimum pressure of oxidizing background atmosphere, needed for depositing manganite films with optimal magneto-transport properties and without necessity of any annealing treatments, is an important experimental difference between MBE and PLD: usually, the background oxidizing gas pressure is much higher in the case of PLD (0.1–1 mbar compared with less than 10^{-5} mbar in the case of MBE) [9,10]. In order to obtain optimised properties in the case of PLD in situ [11] or ex situ [12] oxygen annealings have been used. The physical properties such as the metal-insulator transition temperature, the temperature where the maximum electrical resistivity occurs (T_{MI}), and the colossal magnetoresistance effect (CMR) can be strongly influenced by a modification of the oxygen content due to post-growth annealings [13,14] (for a more complete review on the oxidizing annealing treatment see Ref. [15]).

However, the utilization of high oxygen pressure (about 0.1–1 mbar) during the PLD growth severely restricts the full analytical capabilities of conventional Reflection High Energy Electron Diffraction (RHEED) system for in situ control of growth, though a technological solution at high oxygen pressure (in the range between 0.1 mbar and 1 mbar) [16–19] has been proposed.

In this paper we explore manganite deposition by PLD in the regime of low pressure (lower than 10^{-3} mbar) and low laser fluence, corresponding to deposition rates per pulse $<10^{-2}$ unit cells/pulse, in which the film oxidation occurs primarily as a result of the interaction of the plume

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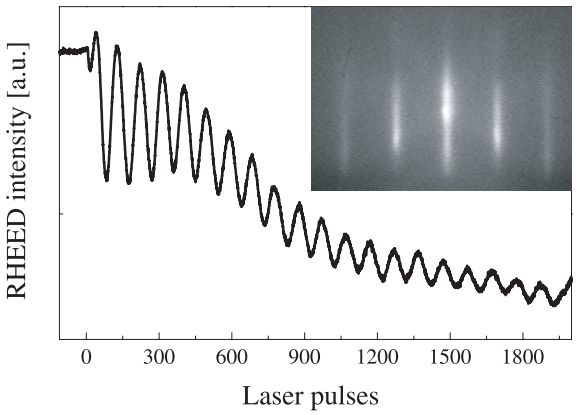

Fig. 1. RHEED intensity oscillations during the growth of a $La_{0.67}Sr_{0.33}MnO_3$ film, corresponding to a deposition rate per laser pulse of 0.042 Å/laser pulse. In the inset the RHEED pattern of a 100 unit cells thick film is shown.

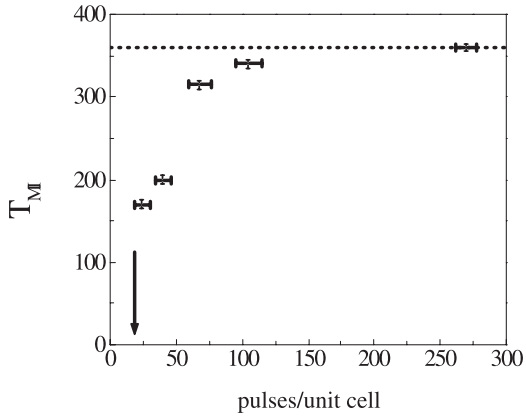

Fig. 2. Resistivity versus temperature for two $La_{0.67}Sr_{0.33}MnO_3$ films grown, respectively at 270 pulses/unit cell (a) and 20 pulses/unit cell (b).

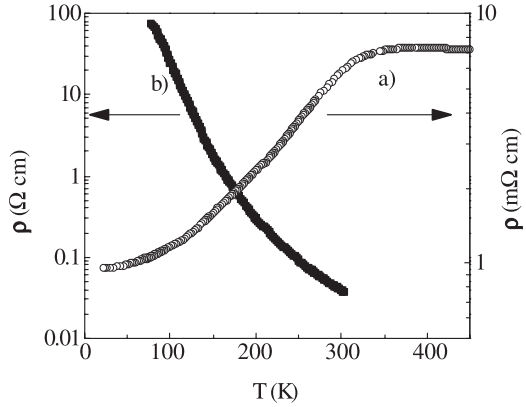

Fig. 3. Metal-insulator transition temperature, T_{MI}, of $La_{0.67}Sr_{0.33}MnO_3$ films deposited by PLD at different growth rates. The arrow pointing to the growth rate of about 20 pulses per unit cell indicates the threshold for the occurrence of the metal insulator transition.

with the background gas. We find that it is indeed possible to deposit high quality manganite thin films by PLD in this regime with atomically flat surfaces, and without the need for any in situ or ex situ post-growth annealing treatment.

2 Experimental details

$La_{0.67}Sr_{0.33}MnO_3$ (LSMO) films deposition was carried out using an excimer laser charged with KrF (248 nm wavelength, pulse width 25 ns), varying the laser fluence between 0.3–2.1 J/cm^2. Substrates (5×5 mm^2 $SrTiO_3$ (001) single crystals) were placed ∼80 mm from the target on a heater at a growth temperature $T_g \sim 650$ °C. The background atmosphere consisted of a mixture of O_2 with 10% ozone. The average background pressure in the chamber was fixed at 5×10^{-4} mbar. The mixture of molecular oxygen and ozone was injected through a narrow nozzle placed in close proximity of the target and pointing toward the plume. After the growth, samples were cooled to room temperature in about 30 min in the growth atmosphere. No post-growth annealing treatments, either in situ or ex situ, were carried out on the films. Reflection High Energy Electron Diffraction (RHEED) was used in situ to monitor the surface quality. Due to the correlation of the RHEED oscillations with the deposition rate per laser pulse [20] it was possible to monitor the growth rate through the intensity oscillations of the RHEED specular spot, for all the films deposited using different laser fluences. As an example, in Figure 1, we show the specular spot RHEED intensity oscillations during the initial stage of the film deposition, corresponding to a deposition rate per laser pulse of about 0.04 Å/laser pulse, obtained using a laser fluence of 0.3 J/cm^2. In the inset of Figure 1 a typical RHEED pattern of a 100 unit cells thick film is shown. The RHEED pattern of all the deposited films showed almost 2D features, independent of the deposition rate per laser pulse used.

3 Results and discussion

All films had the same thickness of 100 unit cells (about 400 Å). The deposition rate per laser pulse was varied whereas all other deposition parameters were left unchanged. For such a thickness the presence of a magnetic and electric "dead" layer [21], can be neglected. The resistivity versus temperature measurements of LSMO films grown at 0.3 J/cm^2, which is near the ablation threshold, show metallic behaviour with T_{MI} as high as 370 K, comparable with the values obtained for the best single crystals (Fig. 2a). T_{MI} gradually decreases as the fluence increases, and films grown at a fluence of 2.1 J/cm^2 showed an insulating behaviour (Fig. 2b). The major experimental finding of our research is the strong dependence of T_{MI} on the deposition rate per laser pulse, shown in Figure 3. In order to check that such an effect could not be ascribed to a wrong cation stoichiometry in films grown at higher deposition rates per pulse, the film composition was confirmed to be equal to the target, La(Sr):Mn = 0.7(0.3):1, by Rutherford Backscattering Spectrometry. Furthermore, the structural quality

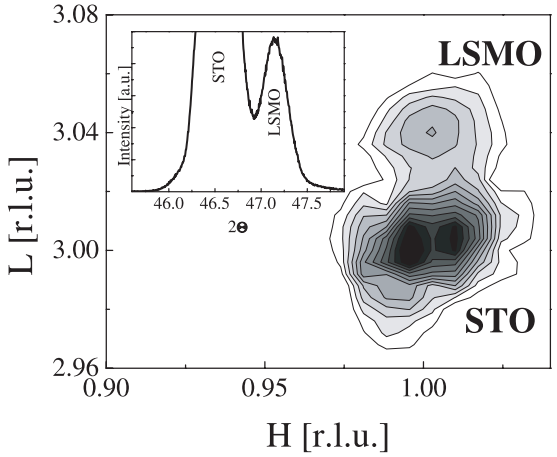

Fig. 4. Isointensity contour plot in logarithmic scale of reciprocal space map around (103) asymmetrical reflection of an optimised LSMO film grown on $SrTiO_3$(STO) substrate. The range of the logarithmic scale is from 18 to 15 000. Inset: (002) symmetrical diffraction spectra.

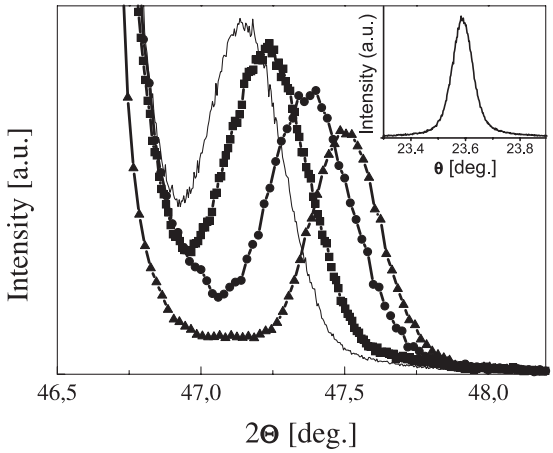

Fig. 5. XRD spectra, of the (002) reflection, for four films deposited at the deposition rate per laser pulse of 1.4×10^{-2}, 3.2×10^{-2}, 6.4×10^{-2}, 1.5×10^{-1} Å/laser pulse, indicated by continuous line, squares, circles and triangles respectively. In the inset is showed the rocking curve of the (002) LSMO reflection for a film deposited at a deposition rate of 1.5×10^{-1} Å/laser pulse.

of films grown at different rates was investigated by X-ray diffraction (XRD) using a standard two-axes $\theta-2\theta$ diffractometer in Bragg-Brentano focusing geometry. An additional axis allows the rotation of the sample around its surface normal. The measurements were performed at the Cu Kα wavelength. The perpendicular and the in-plane lattice parameters were measured by symmetrical and asymmetrical XRD, respectively. In symmetrical configuration the $\theta-2\theta$ spectra also showed a notable size effect, thanks to the high structural quality of the films along the perpendicular crystallographic direction. In asymmetrical configuration H–L reciprocal space maps around the (103) reflection were performed in order to investigate the strain and the epitaxial relationship between film and substrate. All films resulted to be epitaxial relative to the substrate, and no extra phases were detected.

The LSMO films were in plane matched to the $SrTiO_3$ substrate (cubic with $a = 3.905$ Å). According to the tensile stress, the out-of-plane lattice parameters were found to be contracted with respect to the bulk case. In Figure 4 we report the reciprocal space map around the asymmetrical reflection (103) for the optimised film, exhibiting a T_{MI} of about 370 K. Angular variables are transformed in reciprocal lattice units (r.l.u.) and the map is presented in terms of the H, L Laue indices normalized relative to the lattice parameters of the STO substrate. In the inset, the (002) symmetrical reflection has been reported. Within our experimental resolution, we can deduce that the H-index has the same value for the film and the substrate (103) peak, as an indication of the in-plane lattice constant matching. Due to the presence of the tensile strain the lattice parameter perpendicular to the plane results to be about 3.85 Å, as deduced by the (002) reflection and the value of the L-index of the (103) peak of the film in the map. The perpendicular lattice parameter was observed to increase from 3.83 Å to 3.85 Å with the decrease of the deposition rate from 1.5×10^{-1} to 1.4×10^{-2} Å/laser pulse (Fig. 5). Dho et al. [22] found a similar behaviour in the perpendicular lattice parameter of $La_{0.7}Sr_{0.3}MnO_3$ films increasing the background oxygen pressure. Such a behaviour was ascribed to a partial relaxation of the more oxidised films. The crystallographic quality of the films was not affected by the change of the deposition rate per laser pulse, as confirmed by the value of the full width at half maximum of the rocking curve that resulted to be, for all the deposited films, comparable with that of the substrate, smaller than 0.08°. In the inset of Figure 5 the rocking curve of the (002) reflection of the LSMO film, deposited at a deposition rate of 1.5×10^{-1} Å/ laser pulse, is reported as an example.

We ascribe the striking dependence of T_{MI} on the deposition rate per pulse to the different degree of oxidation of the $La_{.67}Sr_{0.33}MnO_3$ films. To prove that interaction between plume and background atmosphere, rather than direct oxidation of the film surface during the deposition process, is responsible for the higher level of oxidation of film deposited at lower laser fluences, we have introduced pauses, several minutes long, after the deposition of each unit cell in order to increase the oxygen diffusion into the film. Several films have been grown in these modified conditions at different fluences, but no increase of T_{MI} has been detected. However, at a background pressure of 5×10^{-4} mbar we should be still in a collisionless, vacuum-like regime, where interaction between plume and background atmosphere is expected to be negligible, with a mean free path of the order of tens of centimetres. On the other hand, the observed interaction effects indicate that the local background pressure in the plume vicinity is at least 10^{-2} mbar, with a mean free path smaller of one centimetre, where frequent collision processes start to occur between the expanding plume and the background gas [23]. A large increase of local background pressure in

the proximity of a thin nozzle has been observed in similar experiments [24].

Calculations in reference [25] have shown that, in the collision regime, the plume front is strongly compressed and a compressed layer of the background gas, in front of the plume, is quickly "snowploughed" by the expanding plume. Under our experimental conditions, the density of the unperturbed background gas can be estimated to be about 10^{14} cm^{-3}. The plume density, estimated from the amount of deposited atoms onto the substrate for each laser pulse, can be estimated to be about 10^{12}–10^{14} cm^{-3} for the deposition rate of 0.02 Å/laser-pulse and 0.4 Å/laser-pulse respectively. These densities were much lower than the background gas density in the compressed layer (about 10^{16} cm^{-3} from Ref. [24]), which moves together with the expanding plume. It is now very likely that strong plume oxidation takes place in the mixing region where the interaction between the ablated material and the background gas is maximum. A demonstration of this effect on a different system is given in reference [26], in which the expansion of an Al plume in molecular oxygen was investigated and the formation of AlO was detected in the mixing region. In these conditions, the expanding plume can drag most of the background gas positioned in front of the plume. As a consequence, the ratio between the density of the background gas and the ablated species, in the mixing region, would be higher in the case of a lower growth rate. Furthermore, in the present case, a larger amount of atomic oxygen is expected in this region as a consequence of the frequent collisions between ozone molecules in the background atmosphere and the high-energy plasma particles. These phenomena can explain why lower fluence, and growth rate, yield higher plume oxidation and consequently higher T_{MI}.

4 Conclusions

In this paper we studied the properties of manganites films, deposited by PLD in low background pressure conditions ($<10^{-3}$ mbar), as a function of the fluence. We have demonstrated the fundamental role played by the fluence in order to optimise the oxidation process of the plume. We have correlated the film oxygen stoichiometry with the fluence, and consequently with the plume oxidization. We have obtained high quality as-grown manganite films using the in situ RHEED diagnostic at low oxygen pressures (10^{-4}–10^{-3} mbar). The resulting films possess a high metal-insulator transition temperature (T_{MI}), without necessity of any further post annealing treatment. We explained the experimental results by a physical model based on the interaction of the expanding plume with the oxidizing background gas.

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