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The effect of the fluence on the properties of La–Ca–Mn–O thin films prepared by pulsed laser deposition

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Abstract

Thin films of $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ were deposited on $SrTiO_3(100)$ by PRCLA (Pulsed Reactive Crossed-Beam Laser Ablation). The dependence of the structural and transport properties of the films on the laser fluence and different target to substrate distances during the growth are studied. Both parameters have a direct influence on the films thickness and velocity of the ions arriving at the substrate, which influence the film properties directly.

The surface roughness of the $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ thin films is depending mainly on the laser fluence and less on the target-substrate distance. Lower laser fluences and therefore lower growth rates yield film with lower roughness, i.e. in the range of 0.2 nm. The electronic transport measurements show a decrease of the transition temperature from metal to semiconductor with an increase of the target to substrate distance. This is related to an increase of the films thickness and therefore decrease of the strain in the films due to the lattice mismatch with the substrate. The magnetoresistance values are also strongly affected by the tensile strain, i.e. they increase for higher strained films.

Keywords: PRCLA; PLD; Magnetoresistance; Manganite

1. Introduction

The manganese oxides with the general formula $RE_{1-x}M_x MnO_3$ (RE = rare earth, M = Ca, Sr, Ba, Pb) exhibit a complex relationship between the structural, magnetic and transport properties. The mixed valence (3+/4+) of the Mn ions in the perovskite structure induces the double exchange interaction within Mn^{3+}–O^{2-}–Mn^{4+} pair, which is used to explain the resistivity and ferromagnetic/metallic properties of the material [1]. In addition to the double-exchange interaction that promotes hopping of carriers, Jahn–Teller splitting of the outer Mn *d* levels was introduced in order to give a complementary explanation for the magnetoresistance effect [2]. A drop in the resistivity has been observed for a doping range of $0.3 < x < 0.7$ in $La_{1-x}Ca_xMnO_{3-\delta}$ at the transition point from metal to semiconductor which is accompanied by the observation of the colossal magnetoresistance effect (CMR) [3]. The change in resistance of manganite films in a magnetic field can be explained by a parallel alignment of the Mn^{3+} and Mn^{4+} spins, which results in a decrease of the resistance, and therefore negative magnetoresistance. The electronic conduction in the manganites is also affected by the oxygen content of the films, due to the change in the valence state of the transition metal [4]. The magneto–transport properties are also sensitive to strain which can be induced in the films by a lattice mismatch with the substrate [3,5]. A possible integration of those materials in device applications based on the sensitivity to magnetic fields represents one of the major tasks for industrial applications, such as magnetic recording. The main goal for applications is to obtain high magnetoresistance (MR) values at temperatures as close as possible to RT.

The $La_{1-x}Ca_xMnO_{3-\delta}$ system exhibits a rich phase diagram depending on the variation of the calcium content. For the doping range $0 < x < 0.4$, the material reveals a metallic conduction and ferromagnetic behaviour at low temperatures

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($T < 250$ K), while at high temperatures ($T > 250$ K) an insulating state and antiferromagnetic behaviour is observed [6].

Pulsed Laser Deposition (PLD) is an established technique for growing oxide thin films, including high temperature superconductors, CMR materials (e.g. manganites), etc. [7,8]. PLD allows the synthesis of layers with different strains depending on the choice of substrate [5] and the films thickness which can be controlled by the number of laser pulses or target-substrate distance. The growth mechanism associated with PLD is rather complex. The substrate temperature affects the atomic surface mobility during the deposition process, leading to the formation of an amorphous, polycrystalline, and finally high quality epitaxial material [9]. In particular, the target to substrate distance is one important parameter that needs to be considered [10] since the species are thermalized in the plume.

For the growth of oxide films, an oxidizing environment is necessary to be maintained during the deposition process in order to form the desired crystal phase at the deposition temperature. One approach to improve the oxygen content in the films was the development of Pulsed Reactive Crossed Beam Laser Ablation (PRCLA), where a synchronized reactive gas pulse interacts with the plasma plume close to the target. Due to the geometry of PRCLA, the high probability of reactive scattering of the plasma with the oxidizing source [11] leads to a fast thermalization of the species which arrive at the substrate resulting in a low probability of re-sputtering of the growing film [12].

The film thickness has a direct influence on the transport properties of the $La_{1-x}Ca_xMnO_{3-\delta}$ thin films, and a relationship between the microscopic structure and the metal to insulator transition temperature has been reported [13]. A decrease of the film thickness increases the strain in films when substrates with different lattice parameters are applied. The strain in thin films can result in a decrease of the metal to semiconductor transition temperature and an increase of the magnetoresistance value [3].

2. Experimental

The $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ (LCMO) thin films were grown on (1 0 0) $SrTiO_3$ substrates, using the Pulsed Reactive Crossed Beam Laser Ablation (PRCLA) method. The experimental setup has been described previously in detail [14]. A cylindrical target of LCMO with high purity (>99.9%) was ablated with a KrF excimer laser ($\lambda = 248$ nm, $\nu = 10$ Hz). The target to substrate distance was varied from 3 to 7 cm while 30 000 pulses with a constant laser fluence of 5.5 J cm^{-2} were applied. Experiments at laser fluences ranging from 2 J cm^{-2} to 8 J cm^{-2} were also carried out. The uncertainty in the measurement of the laser energy is around 5%.

During the deposition process, two different oxidizing sources were used, i.e. O_2 as background gas (at a pressure of $8{*}10^{-4}$ mbar) and N_2O which is used for the gas pulse ($p = 2$ bar, duration 400 μs). The overall pressure in the chamber during the deposition with the gas pulse was 10^{-3} mbar.

X-ray diffraction (XRD) patterns were recorded using a Siemens (D5000) diffractometer, equipped with an Eulerian cradle for texture analysis, in a standard θ–2θ configuration. The surface morphology of the films was studied using an Atomic Force Microscope from Park Instruments. The measurements were performed in contact mode and the root-mean-square roughness (R_{rms}) values were determined over 2 μm × 2 μm scan areas.

The films thickness was measured with an Ambios Technology XP-1 profilometer.

Rutherford Backscattering spectroscopy (RBS) was used to determine the composition of the multicomponent material and the oxygen content in the films. The RBS measurements were performed using a 2 MeV ^{4}He beam and a silicon surface barrier detector at 165 degree. The collected RBS data were simulated using the RUMP software [15].

The resistance of the films was measured using the four-probe method with a Quantum Design Physical Properties Measurement System (PPMS). The magnetoresistance was measured in magnetic fields of up to 5 T.

3. Results and discussions

In general, LCMO films grown on $SrTiO_3$ substrates show a very smooth surface with RMS values varying between 0.15 nm and 1 nm. The AFM images of LCMO thin films deposited on $SrTiO_3$ with different laser fluences are shown in Fig. 1. The average growth rate was calculated as the ratio between the films thickness and number of pulses. With increasing laser fluences, i.e. from 3 J cm^{-2} to 5 J cm^{-2}, the growth rate increases from 0.021 Å/pulse to 0.74 Å/pulse (see Fig. 1). The films grown at slow growth rates (2 J cm^{-2} and 3 J cm^{-2} laser fluence) show a low surface roughness. With increasing laser fluence, the films surface appears to be more dense (case c) but larger grains appear on the surface, resulting in a larger roughness (RMS = 0.4 nm). The laser fluence has therefore a pronounced effect on the particle size and density, for a chosen material and a fixed laser wavelength [16].

For different target to substrate distances at a given laser fluence, no major modifications of the surface morphology were observed.

Atomically smooth surfaces of manganite films at a given laser fluence have been observed previously [17], but also rather rough surfaces are common for epitaxial manganite thin films [18]. The main parameter that contributes to a systematic increase of the surface roughness is the films thickness [3], and it was recently suggested that the film roughness is influenced by strain induced in the film by a lattice mismatch with the substrate [19]. Our AFM investigations reveal that LCMO films can be grown on STO substrates with a low roughness when low growth rates are used.

A possible major advantage of PLD and PRCLA among other deposition methods is the stoichiometric transfer of the material from the target to the substrate. Fig. 2 shows that the composition of the grown films does not change for laser fluences in the range of 2–7 J cm^{-2}. These results are in good agreement with previous studies showing a congruent transfer

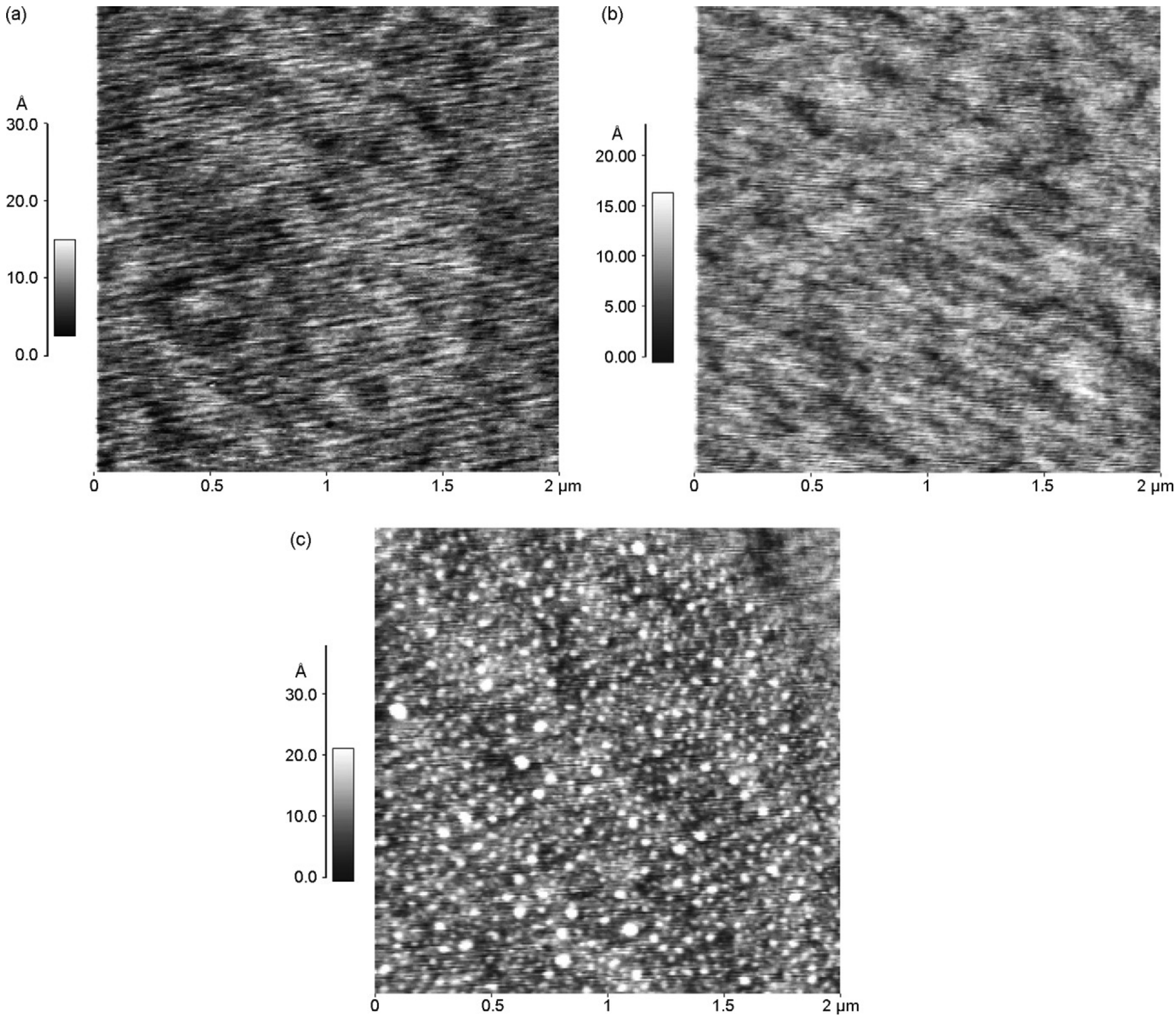

Fig. 1. AFM images of the LCMO thin films deposited on $SrTiO_3$ (STO) at laser fluences of (a) 3 J cm^{-2}, (b) 4 J cm^{-2} and (c) 6 J cm^{-2}. The film roughness (RMS) and growth rate is also included.

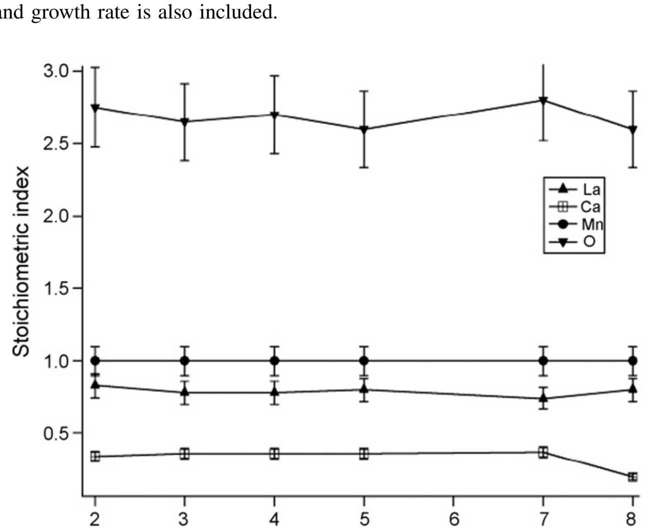

Fig. 2. Composition of the $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ films deposited at various laser fluences.

of $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ [20]. For the highest applied fluence (8 J cm^{-2}) RBS analysis reveal a non-uniform elemental composition through the film. The composition for this thin film is therefore only an average composition over the films thickness.

The RBS analysis reveal also that the films are oxygen deficient (see Fig. 2), with oxygen contents varying between 2.7–2.8.

Therefore, we have chosen a laser fluence of 5.5 J cm^{-2} which yields films with a uniform composition and low surface roughness for the following studies.

The X-ray diffraction patterns indicate an epitaxial growth of the $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ films on $SrTiO_3$ ($a_{p\ STO}$ = 3.91 Å) at a deposition temperature of 650 °C, as shown in Fig. 3.

The films deposited at different target to substrate distances show an epitaxial growth on STO (0 0 1) oriented substrates. The evolution of the lattice parameter as a function of the target to substrate distances and therefore films thickness was also

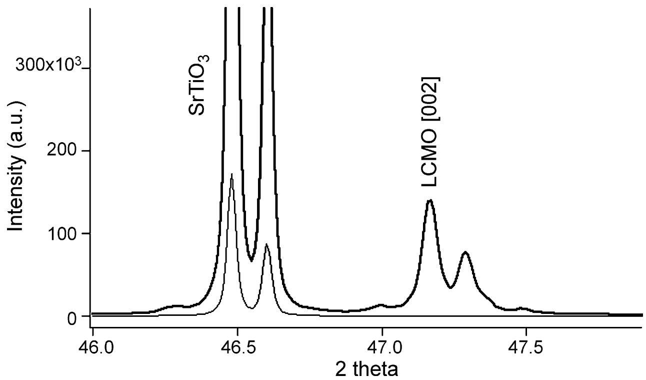

Fig. 3. XRD patterns of an epitaxial LCMO thin films deposited on $SrTiO_3$ with a laser fluence of 5.5 J cm^{-2}. The distance between the target and the substrate was 4 cm and the substrate temperature T_s = 650 °C.

studied. A change of the target to substrate distance results in a change of the films thickness (for a given number of pulses and at a given laser fluence), i.e. a decrease of film thickness with increasing target to substrate distances. The lattice parameters of the LCMO films are very close to the values for the bulk material (3.890 Å) when the substrate is placed close to the target (target- substrate distances of 3 cm). This shows that the films are already thick enough to release the stress over the film thickness. For thinner films (thickness varying between 60–65 nm), i.e. deposited at larger target – substrate distances, smaller lattice parameter, i.e. closer to the values for the substrate material, were obtained, which shows that the thin films are under a tensile strain. The tensile strain leads to a deformation of the pseudo- cubic cell, resulting in an expansion of the lattice parameter in the in- plane direction and compression in the out of plane direction. This is confirmed by a decrease of the out of plane parameter, i.e. the c axis, with a decrease of the films thickness.

Positive values of the lattice to substrate mismatch, corresponding to a tensile strain, are often observed in manganite films grown on $SrTiO_3$ [3].

The temperature dependence of the resistance for the LCMO films deposited on STO was also studied for the films deposited at different target to substrate distances. All films show a semiconductor to metal transition temperature, T_p, with a change of the electrical resistance as a function of the target to substrate distances; the films thickness varies from 380 nm for a film grown at a target to substrate distance of 3 cm to 60 nm for a film grown at a distance of 7 cm. The semiconductor to metal transition temperatures decreases from 112 K to 110 K for films with thickness of 380 to 200 nm respectively and from 107 K and 105 K for films of 65 nm and 60 nm thickness respectively (see Table I). These results are in good agreement with previous reports on LCMO films deposited on STO substrates [13]. As the thickness of the film increases the strain is released and the lattice parameter reaches values close to that of the bulk material. Another important aspect is the oxygen deficiency in the films, which was derived from the RBS measurements, because it leads to a partial reduction of Mn^{4+} to Mn^{3+} resulting in a change in the charge carrier density. The e_g electron hopping in the Mn^{4+}- O-Mn^{3+} chain is reduced, as there are less Mn^{4+} available in the structure. The loss of oxygen leads to a decrease of carrier concentration and an increase in films resistance (~10^6 ohm). This has in addition to the strain in the thin films a direct effect on the transition temperature, i.e. decrease, compared to the bulk material, where the transition takes place around 250 K [6]. The oxygen deficiency will also influence the crystallographic structure, and therefore the transport properties, but this cannot explain the systematic change of the transition temperature with varying target-substrate distances, as the oxygen deficiency is very similar for the different film thickness.

Different misfit values (between substrate lattice and film lattice) and therefore the strain are induced in the structure by different films thickness for a given substrate. The transfer integral, which describes the electrons hopping between the Mn^{3+} and Mn^{4+} ions, can be described by the relation $t \propto \cos(\phi)/d^{3/5}$, where ϕ is the bond angle of Mn–O and d is the bond length [21]. It has been suggested that the tensile strain induced by the $SrTiO_3$ substrate increases the lattice constant by a change in both Mn–O–Mn bond angles and bond lengths [1,22]. Based on this relation, we can conclude that for thinner films, the electron transfer integral is reduced and therefore the transition temperature point, T_p, shifts to lower values.

The temperature dependence of the resistance for the films deposited at 4 cm in magnetic fields of 0 T, 2 T and 4 T, is shown in Fig. 4 and a MR ratio of 20% at magnetic field of 4 T was obtained. The MR ratio is defined as $\rho(H) - \rho(0)/\rho(0) \times 100$, where ρ(H) and ρ(0) are the resistivity of the material in a magnetic field H and without magnetic field.

Table I
Magnetoresistance values (MR) values calculated for layers deposited at different target to substrate distances

LCMO/$SrTiO_3$		
D t-sd(nm)	T_p (K)	MR (%) @120 K
3 cm (380 nm)	112 K	−32% at 5 T
4 cm (200 nm)	111 K	−56% at 4 T
6 cm (65 nm)	108 K	−66% at 5 T
7 cm (60 nm)	105 K	−72% at 5 T

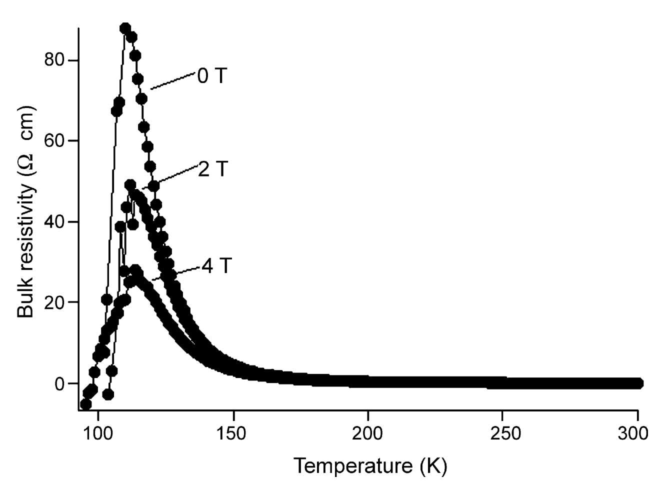

Fig. 4. Temperature dependence of the resistance of a LCMO film deposited at 4 cm target to substrate distance.

The MR ratios (see Table I) of the films are calculated at 120 K, which is above the temperature corresponding to the transition temperature.

Larger MR values are observed for the LCMO/STO system above the transition temperature, Tp. In general, the films grown at larger target to substrate distances reveal higher magnetoresistance values due to the significant strain induced in the crystal structure. Our results are in agreement with previous reports on LCMO layers [13].

4. Conclusions

PRCLA is a suitable method for the growth of $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ (LCMO) films with a stoichiometric transfer of the metals. The $SrTiO_3$ substrates induce a tensile strain in the thin LCMO films. The surface morphology and microstructure of the strained manganites LCMO thin films is depending mainly on the laser fluence and less on the target-substrate distance. Lower fluences and therefore lower growth rates yield films with lower roughness. The transport properties of the LCMO films on $SrTiO_3$ substrates showed that the tensile strain induced by the lattice mismatch with the substrate shifts the transition temperature of the semiconductor to metal transition to lower temperatures. This can be explained by a decrease of the electrons transfer, i.e. the transfer integral, between the Mn ions. The magnetoresistance values measured at temperatures above T_p, are also strongly affected by the tensile strain, i.e. they increase for higher strained films.

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