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Pulsed laser deposition of atomically flat $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films using a novel target geometry

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Received: 29 September 2003/Accepted: 24 February 2004

Published online: 26 July 2004 • © Springer-Verlag 2004

ABSTRACT A new ablation target geometry is presented that was used to produce thin films of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ grown heteroepitaxially on SrTiO_3 by pulsed reactive crossed-beam laser ablation. The films were grown in order to perform angle-resolved photoelectron spectroscopy, which demands that the surface be atomically flat. In situ and ex situ analysis shows that this condition was met, even after depositing to a thickness of over 100 nm.

PACS 61.10.-i; 61.18.Bn; 68.47.Gh; 71.27.+a; 81.15.Fg

1 Introduction

Since the discovery of colossal magnetoresistance in the heavily doped perovskite manganites by Jin et al. in 1993 [1], the physics responsible for this phenomenon has been intensively investigated. A powerful analytical technique is angle-resolved photoemission spectroscopy (ARPES) [2], which can yield important information on the relevant low-binding-energy electronic states such as those responsible for the double-exchange hopping mechanism along the Mn–O chains [3]. However, the experimental determination of the electronic structure via ARPES is only possible with a perfect sample surface. This is because only the parallel component of the photoelectron's momentum vector k is preserved as it escapes the sample surface; hence the surface and crystallographic orientations relative to the detector must be well defined.

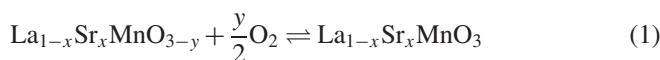
It is exceedingly difficult to prepare a clean and crystallographically unique surface by in-vacuum cleaving of perovskite structures; this is due mainly to their isotropic cubic symmetry. Preparation of high-quality heteroepitaxial films in situ is therefore an exciting alternative approach.

One of the most intriguing aspects of strongly correlated electron systems, such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, is the influence of the degree of doping (x) on the electronic properties. Pulsed laser deposition (PLD) has been shown to be a very attractive film growth technique for such chemically complex materials due to its ability to faithfully transfer the stoichiometry

of the bulk target to the growing film [4]. Normally, therefore, an investigation of the effect of doping on the physical properties of the films would require a set of target materials covering the doping region of interest. In this paper, we present results for the growth of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ by pulsed reactive crossed-beam laser ablation (PRCLA) [5], whereby x could be chosen at will between 0 and 1 without the need to change the target [6].

2 Experimental setup

The experimental setup has been described comprehensively elsewhere [6, 7]. Briefly, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films were deposited in an ultrahigh vacuum chamber (base pressure 7×10^{-9} Pa) by ablating a target rod composed of a section of LaMnO_3 (LMO) and one of SrMnO_3 (SMO) using the fourth harmonic of a Nd : YAG laser (10 Hz, 266 nm, 5 ns, 2 J cm^{-2}) in the presence of a synchronized N_2O gas pulse (average pressure 2×10^{-2} Pa). N_2O was chosen as the primary oxidizing gas due to its enhanced ability over O_2 in oxidizing Mn [8]. O_2 was also bled into the chamber (1.5×10^{-2} Pa) to force the equilibrium of the reaction



toward full oxidation of the deposited film [9]. Films were deposited on $10 \times 10 \text{ mm}^2$ atomically flat $\text{SrTiO}_3(001)$ substrates at 750°C .

A 100 nm film would typically require 46 000 laser shots. The doping x was set by the ablated lengths of each section l_{SMO} and l_{LMO} . The rod was translated at 28 mm s^{-1} , and $l_{\text{SMO}} + l_{\text{LMO}}$ was typically 40 mm. A complete target stroke cycle was thus completed in about 3 s (30 laser pulses), significantly less than the time required to deposit a complete monolayer. This ensured alloy growth [6].

The deposition apparatus was adapted to be compatible with the ARPES station at the Surfaces and Interfaces Spectroscopy beamline at the Swiss Light Source.

The films were analyzed in situ during and after deposition using reflection high-energy electron diffraction (RHEED). The films were analyzed ex situ for their chemical composition by Rutherford backscattering spectroscopy (RBS, 2 MeV $^4\text{He}^+$ ions) and for their crystallinity using X-ray diffraction ($\text{Cu } K_\alpha$ radiation plus a Ge(220) double crystal monochromator). The temperature dependence of the film resistance was

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studied using a temperature-controlled four-point resistance setup.

3 Results and discussion

The film quality could be monitored during growth using RHEED. There was no evidence of intensity oscillations of the specular (00) reflection, though, as the two-dimensional diffraction zero-order and first-order Laue zones remained throughout the entire deposition (Fig. 1), it can be concluded that the films grew in a step flow mode. Kikuchi lines could also be seen throughout growth, which is indicative of high crystalline purity.

Heteroepitaxial growth was further confirmed ex situ by X-ray reflectivity and diffraction. The low-angle reflectivity curves showed clear Kiessig fringes that could be fitted to a film roughness of less than 1 Å, even for films grown to

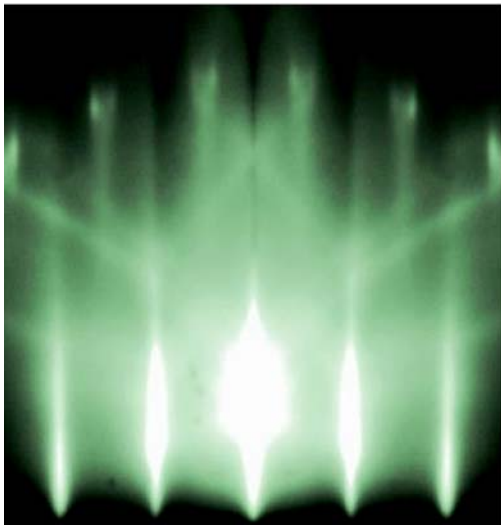


FIGURE 1 RHEED image of a 130 nm-thick $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ thin film along the (100) azimuth. Note the 2-D zero-order and first-order Laue zone spots and the strong Kikuchi lines

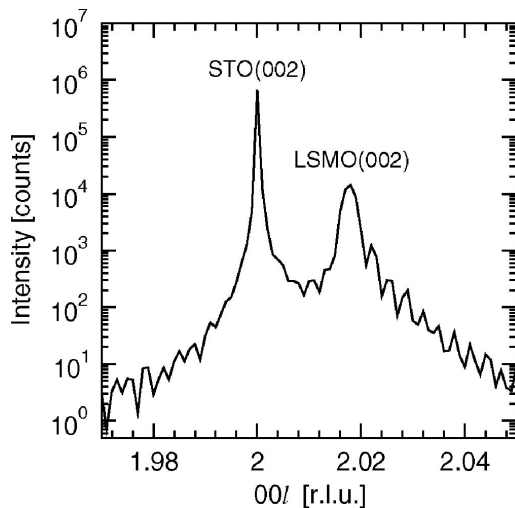


FIGURE 2 $\theta-2\theta$ XRD pattern of a 130 nm-thick $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ thin film. The x -axis is given in reciprocal lattice units (r.l.u.) of the SrTiO_3 substrate system. Note the Kiessig fringes

a thickness of 130 nm. The fringes were also seen in the $\theta-2\theta$ spectra, which only showed (00 l) reflections of the substrate and film (Fig. 2). The out-of-plane lattice constants for $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ and SrTiO_3 were determined to be 3.870 Å and 3.905 Å, respectively. The film is therefore tetragonally distorted with a shortening of c compared to the bulk value of 0.15%, due to the anisotropic strain induced by the lattice mismatch in-plane of +0.7%.

The RBS data are summarized in Fig. 3. In addition to allowing one to determine the film stoichiometry, channelling experiments yield information on the film quality, especially the density of crystallographic faults (e.g., edge and screw dislocations) with a sensitivity excluded to laboratory-based XRD. The films showed the maximum degree of channelling possible for the experimental setup, with a χ^2 -value of only 3% (Fig. 3a). The slopes of the substrate and film peak tops are identical, which implies that their crystal quality is the same. The change in stoichiometry as a function of the ratio of ablation length of the two components of the target $l_{\text{SMO}}/l_{\text{LMO}}$ is given by

$$x = \frac{Q_{\text{SMO}} l_{\text{SMO}}}{Q_{\text{SMO}} l_{\text{SMO}} + Q_{\text{LMO}} l_{\text{LMO}}} \quad (2)$$

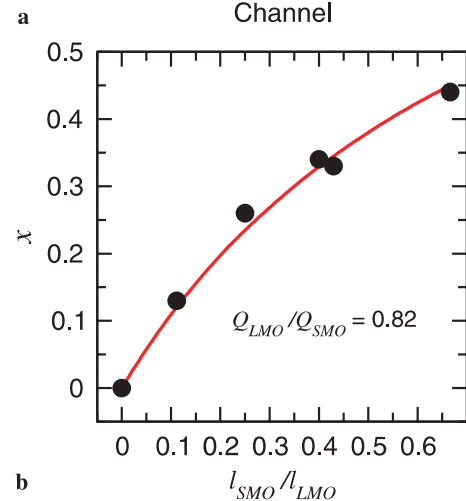
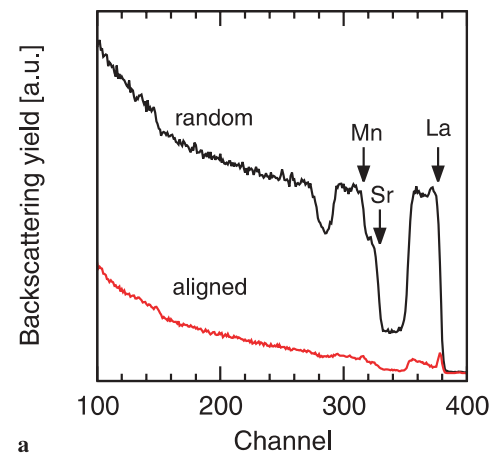


FIGURE 3 **a** Randomly oriented and channelled (aligned) RBS spectra of a 130 nm-thick $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ thin film. **b** The change in film stoichiometry (x) of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ films as a function of the target length ratios $l_{\text{SMO}}/l_{\text{LMO}}$. The best-fit curve using (2) yields a deposition ratio of $Q_{\text{LMO}}/Q_{\text{SMO}} = 0.82$

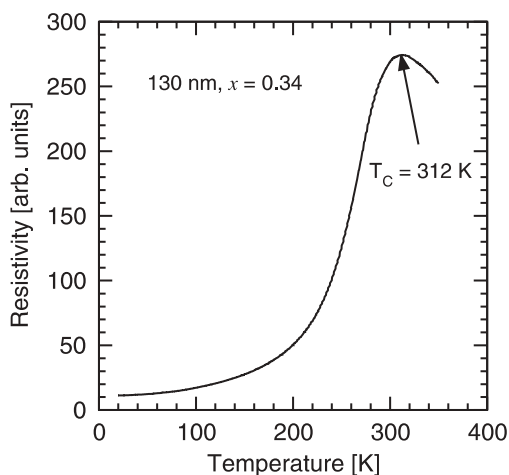


FIGURE 4 Four-point resistance measurements of a 130 nm-thick $\text{La}_{0.66}\text{Sr}_{0.34}\text{MnO}_3$ thin film as a function of temperature. The transition Curie temperature was 312 K

and can be fitted to a relative deposition yield of the components $Q_{\text{LMO}}/Q_{\text{SMO}} = 0.82$ [6] (Fig. 3b).

The film resistance as a function of temperature for $x = 0.34$ is shown in Fig. 4. It has a Curie temperature of 312 K, which lies some 50 K below the bulk value. This has been observed elsewhere [10–12] and is in agreement with finite-size scaling theory. Indeed, another film with a thickness of 106 nm showed a Curie temperature of 280 K.

4 Conclusions

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films have been grown heteroepitaxially on SrTiO_3 using PRCLA and a novel ablation target geometry that allows any degree of doping between $x = 0$ and 1. The films were shown to be atomically flat, with a roughness of around 0.25 of a unit cell. Ion channelling demonstrated that the density of crystallographic defects was as low as that found in the SrTiO_3 substrate. The films should therefore be suitable for high-resolution ARPES measurements.

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