Bidimensional X-ray Diffraction Analysis for Structural and Microstructural Characterization of Lanthanum Manganite Thin Films

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Sodium-doped lanthanum manganite thin films were deposited by Rf-magnetron sputtering onto Si(100) single-crystal substrates. Structural and microstructural properties of both as-deposited and annealed samples were investigated by means of X-ray bidimensional microdiffraction. Two distinct preferred orientations have been detected as a result of the formation of two layers during the growth process. A new method (*Debye ring analysis for stress measurement*, DRAST), based on the analysis of Debye ring distortion, allowed the strain associated with the preferentially oriented domains to be evaluated.

In recent years, several efforts have been focused on the attempt to improve the low-field magnetoresistance (LFMR) effect exhibited by polycrystalline manganites. Such an effect takes advantage of the spin-polarized electron scattering arising at grain boundaries[1] and can be enhanced in many ways, for instance, through the formation of insulating secondary phases (e.g., SiO_2) interconnecting manganite crystallites.[2] Among the essential goals to be reached in order to produce thin-film manganite devices, a special role is played by the control of both strains and grain orientation.[3−6] Transmission electron microscopy (TEM) is a well-known technique for the accurate investigation of these aspects, and synchrotron X-ray micro-diffraction has recently been proved to be a powerful tool to achieve the local mapping of grain boundary strains of strontium-doped lanthanum manganites.[7] Although very important, both these techniques suffer some drawbacks; the former is destructive, whereas the latter cannot be applied to routine experiments. On the other hand, laboratory bidimensional X-ray diffraction (XRD2) is a very promising technique for a ready and effective characterization of different kind of materials both from the structural and the microstructural point of view.[8] Thanks to this technique, a new method (*Debye ring analysis for stress measurement*, DRAST) to assess residual stress by analyzing XRD2 images has been proposed.[9] The main advantage of the DRAST method is related to the possibility to extract structural as well as strain information from a single measurement, and this method has recently been used to evaluate residual stress in perovskite thin films.[10] Thus XRD2 spectra can be analyzed not only to identify the phases of the sample but also to deepen some details concerning its microstructure. These information are invaluable when the functional properties of the materials under investigation have to be optimized.

This letter reports the investigation of structural and microstructural features exhibited by optimally sodium-doped lanthanum manganite ($La_{0.85}Na_{0.15}MnO_3$) thin films grown by Rf-magnetron sputtering onto Si(100) single-crystal substrates; the substrate choice is related to the technological importance of integrating manganites with silicon-based devices.[11] In particular, the study was focused on samples deposited at 700 °C: two samples (A and B) were grown for 60 min. Sample B was annealed at 850 °C for 2 h in a quartz tube in which oxygen was flown and then it was quenched to room temperature. The deposition rate for both samples A and B was 0.25 nm/min. Further details concerning the synthesis of lanthanum manganite thin films have been reported elsewhere.[12,13]

XRD2 images of the as deposited (A) and annealed (B) samples were collected with a D/Max-RAPID Rigaku micro-diffractometer, equipped with a bidimensional image plate detector. The incidence angle was 10°, and the collimator diameter was 300 μm. From the 2θ peak positions, it was possible to identify a cubic structure[14] with different lattice parameters (0.3884(4) and 0.3863(6) nm for samples A and B, respectively). According to previous studies,[12,15] the shrinkage exhibited by sample B can be attributed to the thermal treatment being carried out in an oxidizing environment. Furthermore, annealed samples are slightly flattened along a $[111]_c$ direction, approaching the rhombohedral distortion exhibited by the target powder sample ($La_{0.85}Na_{0.15}MnO_3$). Magnifications of the XRD2 images are reported in Figure 1. It can be noticed that the intensity is not constant around the ring, indicating a significant preferred orientation in both samples. It was reported that the growth of polycrystalline lanthanum manganite on Si(100) produces [110]-oriented thin films.[16] However, the microstructure of sample A cannot be interpreted by a single orientation model: indeed the modulated intensity along the (110) Debye ring at about 32.6° (2θ) shows three maxima. In the case of [110]-preferred orientation, only two maxima at $\Psi = 0°$ and $\Psi = 60°$ (where Ψ is the angle between the sample normal and the normal to the diffracting plane) should be found. Thus the existence of three high-intensity regions reveals the presence of another preferred orientation in the film; in particular, in addition to the [110] orientation, the Debye ring also shows the contribution of the [100] orientation indicated by a maximum of the (110) reflection at $\Psi = 45°$. This is confirmed by the fact that the (100) ring shows a maximum at $\Psi = 0°$ (see Figure 1). Therefore we conclude that two preferred orientations are present in the film. To understand the spatial distribution of the two preferred orientations, XRD2 patterns were collected

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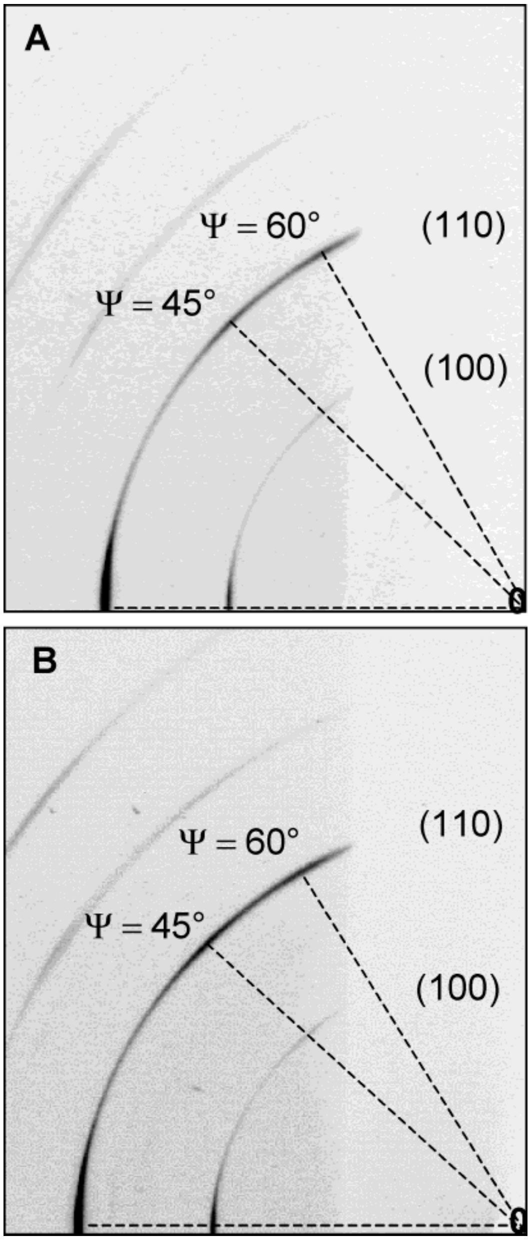

Figure 1. Magnifications of XRD2 images of the (110) reflections located at about $2\theta = 32.6°$ (samples A and B).

at two different incidence angles (1 and 16°). The intensity distribution of the peak at about $2\theta = 32.6°$ for different oriented planes were analyzed integrating the Debye ring ($\Delta 2\theta = 4°$) and plotting the intensities vs ψ (Figure 2). It is clear that the intensity at $\Psi = 45°$ increases in the case of a high incidence angle (16°), and on the contrary, the intensity at $\Psi = 0°$ and $\Psi = 60°$ is higher for low X-ray penetration depth (incident angle = 1°). These data suggest that the differently oriented domains are, indeed, layered; at the substrate interface, the film grows with a [100]-preferred orientation, while the upper layer is [110] oriented. Therefore the substrate seems to promote the [100] growth; beyond a critical thickness, this orientation is overwhelmed by relaxation mechanisms that come along with the novel [110] preferred orientation. Evidences of changes from random to *c*-axis orientation have been reported by Yoo et al.[17] in the case of $YMnO_3$/Si(100) thin films as a results of quenching procedure. Thus, in addition to the film/substrate lattice mismatch, the strains produced during the cooling process can induce the differential layering.

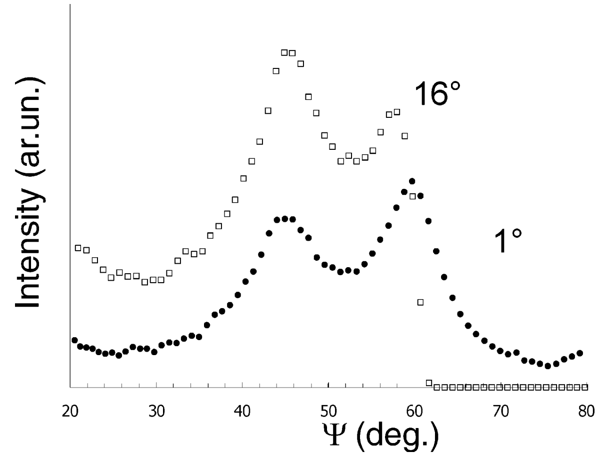

Figure 2. Intensity distribution of the peak at $2\theta = 32.6°$ for sample A. The data were obtained integrating the corresponding Debye ring for all plane directions (ψ). The measurements were carried out at two different incident angles (1 and 16°) to point out the different contribution of two preferentially oriented domains.

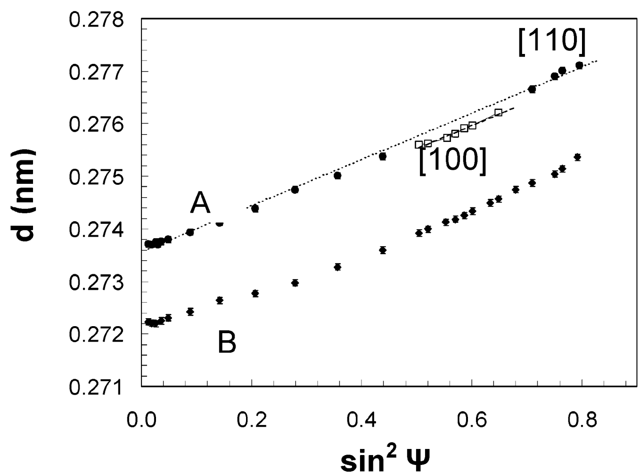

Figure 3. $d \sin^2 \psi$ plots for the samples A and B (incident angle = 16°). The error bars are comparable to the experimental point size. In sample A, two different linear regressions were calculated for [110]- and [100]-oriented domains (R^2 values are 0.9974 and 0.9809, respectively).

Figure 3 shows the $d \sin^2 \psi$ plots of both the as deposited and annealed samples (A and B, respectively), calculated following the DRAST method.[9] The distortion of the Debye ring-diffraction cone can be used for stress calculations and from the analysis of XRD integrated patterns a $d \sin^2 \psi$ plot has been obtained.[18] In sample A, the contributions of the differently oriented domains can be distinguished. The $d \sin^2 \psi$ plot points can be fitted by two straight lines, one referring to the [110]-oriented domains, the second one referring to the [100]-oriented domains ($45 < \psi < 55°$). The slope values of the linear regressions, which are proportional to the in plane stress value, are similar (the calculated lattice strain is about 4%), while the intercepts at $\psi = 0$ are significantly different for the two preferentially oriented domains as well as for the annealed sample (B). This may be due to different structural defects, such as cationic deficiency on La and Mn sites, depending on the annealing temperature and or on the Na occupancy of both La and Mn sites. In the $d \sin^2 \psi$ plot relative to the sample B, the curvature appearing in the range $25 < \psi < 40°$ might be due to the presence of microstructural effects. Actually, the lattice mismatch between the film and the substrate causes micro- as well as macrostrains. It is reasonable that structural relaxation mechanisms (e.g., formation of misfit dislocations at film/substrate interfaces) should be active to relieve these strains.[19] As a matter of fact, epitaxial stress does not contribute to residual stress but produces this kind of structural effects.

On the basis of 2D diffraction experiments, the mismatch between the film and substrate structure in $La_{0.85}Na_{0.15}MnO_3$ thin films, deposited on Si(100) substrates, give rise to strains. The epitaxial strains are possibly relaxed by defect formation. By means of the DRAST method, the strain in the films has been calculated and it has been found that residual strains are only slightly relaxed by thermal annealing. Other structural (defect formation) and strain effects were separately analyzed by means of XRD2. In the "as-grown" film, the presence of two different preferred orientations determines the formation of two layers. At the interface with the substrate, the film is [100] oriented, while the upper layer is [110] oriented. Moreover, the thermal treatments are not significantly effective for strain relaxation, which leads to the decrease in defect concentration. Further developments will be addressed in the comparison between XRD2 measurements and magnetic data; magnetic force microscopy experiments are in progress in order to investigate the extension of ferromagnetic domains and the dependence of magnetoresistive response on both the stress state and the grain orientations.

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