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Microstructural properties of solution-deposited La$_{0.7}$Sr$_{0.3}$MnO$_3$ and LaMnO$_3$ thin films

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The microstructural properties of solution-deposited La$_{0.7}$Sr$_{0.3}$MnO$_3$ and nondoped LaMnO$_3$ films have been studied. Several factors such as the choice of substrate, method of surface cleaning, annealing atmosphere, and precursor solution concentration were considered. Films with smoother surfaces were observed on SrTiO$_3$ (100) and LaAlO$_3$ (100) crystals, due to the near matching of the film-substrate lattice constants and thermal-expansion coefficients. In contrast, substrates such as Si (100) yield films with a rougher morphology. Variations in the crystalline quality and surface morphology of the films were demonstrated, simply by altering the precursor solution concentration and the surface condition of substrate. The local structure of the films was studied by Raman spectroscopy, which indicated enrichment in the oxygen content, differing from ideal oxygen stoichiometry (or from films annealed in inert gas atmosphere). This latter effect was shown to be more effective in the case of LaMnO$_3$, where a structural transition from rhombohedral to orthorhombic was observed by changing the annealing atmosphere from ambient air to pure N$_2$ gas, and is suggested to be the main origin of the anomalous conductivity increase reported in the literature in air or O$_2$-annealed manganite films with respect to stoichiometric bulk La$_{0.7}$Sr$_{0.3}$MnO$_3$. © 2006 American Institute of Physics. [DOI: 10.1063/1.2164534]

I. INTRODUCTION

Doped rare-earth manganites with the general formula of R$_{1-x}$A$_x$MnO$_3$ (R: trivalent rare earth and A: divalent alkaline earth) have attracted much attention in the last decade or so, due to their unique and versatile properties, such as colossal magnetoresistance (CMR) and gas sensing. Nevertheless, several factors such as the requirement of large magnetic fields, to observe the CMR effect, make the realization of their full potential a rather slow process, and therefore, there are intensive efforts ongoing to optimize the properties of these manganites.4,5 One group of the mostly studied manganites is the La$_{1-x}$Sr$_x$MnO$_3$ (LSM), especially as thin films, grown by alternative techniques.6–9 In bulk and at x=0.3 the material becomes a ferromagnetic metal at room temperature (RT) and its Curie temperature is only ~50 K above the RT.2 Solution (or sol-gel) deposition is a technologically recognized method for large area film fabrication, providing an easy control on the film composition and properties as well as being an inexpensive technique. However, there is still a need to describe the factors affecting the microstructural properties of sol-gel-deposited manganite thin films. For example, Manabe et al. prepared epitaxial LSM films (x =0–0.3), behaving metallic below RT (for x =0.1), by the sol-gel method, nevertheless they reported an absence of the anticipated giant magnetoresistance (GMR).10 However, it can be seen from the reported phase diagram and magnetoresistance values for bulk LSM (Refs. 2 and 9) that, for x below ~0.16, the material remains as an insulator (at all temperatures), and that the GMR effects become readily observable as soon as x reaches to 0.175 in the “metallic” doping range (both at and below the RT).

In this work we chose to study sol-gel-deposited films with compositions La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSM30) and LaMnO$_3$ (LM), and aimed to investigate the effects of several factors, such as the film/substrate lattice mismatch, substrate pretreatment, solution concentration, and annealing atmosphere, on their microstructural properties, such as the surface roughness, crystallinity, and stoichiometry.

II. EXPERIMENTAL Procedure

Several substrates including (100)-oriented SrTiO$_3$ (STO), LaAlO$_3$ (LAO), Si single crystals, and polycrystalline, (111) preferentially oriented Pt layers (grown on Si, Inostek, Seoul, Korea) were used for film deposition. STO and LAO crystals have the lattice constants $a_{\text{STO}}$=3.91 and $a_{\text{LAO}}$=3.79 Å, respectively, which closely match that of bulk LSM ($a_{\text{LSM}}$=3.89 Å), and theoretically can allow the growth of single crystalline, epitaxial films. On the other hand, films on Si ($a_{\text{Si}}$=5.43 Å) and polycrystalline Pt ($a_{\text{Pt}}$=3.92 Å) are naturally expected to be polycrystalline. Prior to the sol-gel deposition, most substrates were subjected to a selected cleaning procedure, such as heating at high temperatures, washing in a buffered hydrofluoric acid solution (BHF) as in the case of Si, etc., in order to remove the surface adsorbents and native oxides, to enable a uniform film growth on them, as well as to observe the effects—if there are any—of these processes on the microstructure of the films. For Si, the oxidation temperature is 900–1200 °C and thus it may be possible to desorb the surface species below these temperatures, without oxidizing the substrate. Indeed, at times when this

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method was employed the films were seen to grow more homogeneously and with high fidelity. Moreover, for Si substrates, somewhat less effective but similar results were obtained via rapid cleaning in chemical solutions. In this case, Si was first immersed in a “piranha” etch (50% H$_2$O$_2$:50% H$_2$SO$_4$) for a few seconds, in order to remove larger surface species, and after rinsing in (DI) water it was washed several minutes in a BHF solution (3–6 vol% HF in water) to dissolve the surface oxides along with the other contaminants.

The LSM30 films were grown by spin coating of precursor solutions prepared by dissolving appropriate (molar weight) ratios of lanthanum nitrate, manganese acetate, and strontium acetate in an acetic acid/water mixture, either at a concentration of 0.4 or 0.25 mol/l. Precursors were colorless, homogeneous, and stable. An initial slow spin rate of 500 rpm for 8 s was followed by 5000 rpm for 30 s during spinning. After each layer deposition, the sample was heated at 400±50 °C, for 10 min, in order to evaporate the solvent out of the film (pyrolysis). A final annealing performed at 800±5 °C, for 10 min and in air, i.e., at ambient oxygen partial pressure, was enough for the full crystallization of the film. Specimens with several successive layers reaching a total thickness of $d =$ ~ 300 or 100 nm were then used for the analysis.

Atomic force microscopy [(AFM), nanostation SIS, Germany] combined with an image processor (SPIP, version 2.3, Image Metrology) was used to obtain the topographical three-dimensional (3D) images and to determine the respective surface roughness (root mean square $S_q$) values along with grain sizes. The phase and crystallinity of the films were investigated by means of x-ray diffraction [(XRD), Cu Ka, $\lambda =1.5418$ Å], in grazing incidence [(GI), grazing angle of 2°] and in conventional O-2O configurations, respectively, in a Seifert 3000 PTS 4-circle diffractometer. Further micro-structural characterization and stoichiometric analysis of the films were performed by utilizing Raman spectroscopy. The Raman spectra (RS) were collected in a backscattering geometry using a Dilor X-Y spectrometer and the 514.5 nm line of an Ar$^+$ laser as the excitation source. The total laser power was kept, in most cases, as high as 30 mW on the sample while the temperature was reduced down to 20 K since these conditions allowed obtaining of a reasonable signal/noise ratio and stronger and better-resolved RS (in contrast with room-temperature data), respectively.

### III. RESULTS

Figure 1 gives topographical (5 × 5 μm$^2$) AFM images of the films (LSM30) deposited from a 0.4 mol/l solution on different substrates. The film on Si shows the greatest roughness of all, and this is followed, in a decreasing order, by those on Pt, STO, and LAO, respectively. While rather smooth surfaces can be seen from the LAO and STO samples in Figs. 1(a) and 1(b) ($S_q =$13.2 and 14.9 nm, respectively), films on Si and Pt [Figs. 1(c) and 1(d)] present many outgrowths, bearing a rougher topology, respectively, with $S_q =$30.9 and 23.3 nm. Also the z-scale variations in Fig. 1 can provide a similar and comparative idea about the morphology of these samples. The determined grain sizes (Table I) also fall in line with these observations. Here we note that an arbitrary change in the “minimum-grain-size” parameter used for size calculations by the used software (as the lower limit), for the Pt and Si samples, provides two different average grain sizes, due to the bimodal nature of the grain growth in these films. It is, therefore, reasonable to suggest that the 200–300-nm-sized large grains in Fig. 1 correspond to large agglomerates in these samples.

The effect of solution concentration (alone) on the film roughness is demonstrated in Fig. 2. Here a film deposited from a 0.25 mol/l solution ($d =$350 nm) shows a dramatic improvement, in terms of surface smoothness ($S_q =11.4$ nm), compared with that deposited from a 0.4 mol/l solution and given in Fig. 1(c).

Figure 3 shows GI-XRD spectra for the samples presented in Fig. 1 and that of a counterpart powder sample (LSM30, synthesized also in air). The formation of a pure perovskite phase in all the films is evidenced by the good agreement in the position of their peak reflections with those of the powder sample (and with the available XRD library files), as well as by the lack of the appearance of any secondary phase or pyrochlores (within the experimental error ~5%). Moreover, replication of all the peaks of the powder (indexed assuming a pseudocubic structure) in the thin-film spectra indicates a polycrystalline nature for all of the films. Here we note that the (00l) reflections, neither for the (bare) LAO and STO crystals nor for the LSM films, were not observable by the grazing-incidence technique. On the other hand, variation in the crystallinity of the latter films can be demonstrated simply by combining the effects of substrate

![FIG. 1. Representative 5 × 5 μm$^2$ AFM images of 300-nm-thick, polycrystalline LSM30 films deposited on LAO (a), STO (b), Si (c), and (111)Pt (d) using a 0.4 mol/l solution. Films on Si and Pt display a nearly equal but much greater roughness than others.](image-url)
cleaning and reduced solution concentration (Fig. 4, see Discussion). If the films on the crystals were epitaxial normally one would not expect to see peaks other than the (00l) ones (in the conventional Θ-2Θ XRD scans).

Figure 5 gives the RS of the films given in Fig. 1 (except the STO sample, see below). These spectra are characterized with a sharp peak near 425 cm\(^{-1}\) and two broadbands at \(\sim 190\) and \(\sim 640\) cm\(^{-1}\). The latter of the broad features is somehow not so strong in the LAO sample compared with the other spectra, but this probably can be understood by analyzing the spectrum of a bare LAO crystal (see also Fig. 5). A strong fluorescence background contributes especially at higher frequencies due to the LAO substrate. In addition to these features, other substrate-related sharp Raman peaks can be seen at 520 cm\(^{-1}\) (Si) and at 145, 471, and 487 cm\(^{-1}\) (LAO), respectively. However, in the case of the STO sample, an enormous (Raman) contribution in the whole spectral range given in Fig. 5 due to the bulk crystal precluded discerning of the Raman-scattering peaks from the film. Nevertheless, it becomes clear by the analysis of the 425 and 190 cm\(^{-1}\) film-related features and of their background in Fig. 5 that these films can be tentatively said to possess a La:Sr ratio of 7:3 and the typical pseudocubic, rhombohedral structure of the \(x=0.3\) doped LSM. These results are in line with the RS reported in the literature for thin films (formed by various techniques\(^{11,12}\)) and bulk single crystals\(^{13,14}\) of LSM30. However, the appearance of the band at \(\sim 640\) cm\(^{-1}\) was not observed by many others. Only a few studies on LSM thin films reported a similar Raman band and usually attributed it to an oxygen nonstoichiometry in the form of La\(_{2}\)Sr\(_{1-x}\)MnO\(_{3+y}\) present in their films.\(^{11,15}\)

Therefore, in order to monitor the progress of the Raman spectra with the doping (\(x\)), we deposited several other LSM films, with \(x=0, 0.1,\) and \(0.2\), also on Si, under similar conditions to the above (described for LSM30 films). The RS collected from these films is shown in Fig. 6, along with the spectrum of the \(x=0.3\) film from Fig. 5. As can be seen, the most composition-sensitive Raman peak is found in the lower frequency region of the RS (between 300 and 190 cm\(^{-1}\), see below), and it indicates a successive doping variation among our solution-deposited films. Here we note that the position and variation of this peak qualitatively agree with those reported for LSM single crystals (of the corre-
For stoichiometric LaMnO₃, the structure is orthorhombic, bearing strong Jahn-Teller distortions. During the rapid cooling process that the solution-deposited amorphous film is heated to a high temperature (e.g., 800 °C), for crystallization, the film lattice will be able to match that of both LAO and STO (there compressive and tensile stresses are expected, respectively). During the rapid cooling process applied here, the STO crystal will shrink a little more than the LAO crystal, which can result in a rougher morphology in the LSM films, as can be seen in Table I. Therefore, it seems that if the cooling of the sol-gel-deposited films is performed very slowly, after crystallization, the film quality can be improved. But, it becomes also clear from an analysis of the substrate parameters for the present Pt layers (Table I) that the crystalline state of the substrate, i.e., whether single- or polycrystalline, has a substantial influence on the film quality. Although Pt has fairly close TEC and lattice-constant values to those of LSM, since in the present work we used (oriented but) polycrystalline Pt layers, the roughness of the films grown on them showed much rougher topology than those on STO or LAO. The Si film displayed the greatest \( S_q \) of all, and this can be understood from the farthest match of its structural parameters with that of LSM (see Table I).

In Fig. 4, the improvement in the film quality, i.e., from poly- towards single-crystalline structure, can be understood by monitoring the change in the relative intensity of the pseudocubic (110) peak [with respect to the (001) substrate/film peaks]. For monocrystalline, commensurate films it would be expected that the film-substrate XRD peaks would simply overlap and that no other reflection peaks could be seen from the films. Nevertheless, it can be inferred by comparing the spectra in Fig. 4 that the usage of less-
concentrated precursors and of well-cleaned substrates may lead to films of higher quality [as in Fig. 4(a)]. It is considerable that the (sharpness) status of the film-substrate interface may be of critical importance in limiting the formation of defective (columnar) regions, which are commonly observable in rather thick ($d \gg 30 \text{ nm}$) manganite films (on even lattice-matching substrates\textsuperscript{21}). Nevertheless, more dedicated studies, such as (cross-sectional) high-resolution electron microscopy, x-ray photoemission spectroscopy, etc., are required to get a better view and control of the interface quality and its effect on the “average” structure (seen by the XRD techniques) of the sol-gel manganite thin films.

Here we discuss the Raman spectral features of the (air-annealed) sol-gel LSM films. In Fig. 6(b), at $x=0.3$ while the peak position of the film ($\sim 190 \text{ cm}^{-1}$) is adjacent to those observed from single crystals (at 5 or 300 K), an increasing disagreement emanates upon reducing $x$. Since line 3 (the present data) was obtained at 20 K, it is normally expected to lie in between those given as lines 1 and 2 (from Ref. 14), provided that the material structure and stoichiometry are identical. It is possible to argue that the high laser power involved (in this study $\sim 30 \text{ mW}$ on the sample) causes some heating of the sample, and perhaps (as suggested in Ref. 22) results in a local variation in the oxygen stoichiometry. Upon reduction of the temperature from 300 to 5 K, only a blue-shift of $\sim 20 \text{ cm}^{-1}$ is expected for this peak for all compositions for $x=0-0.3$ [see Fig. 6(b), lines 1 and 2].\textsuperscript{14} However, the peak frequency data on line 3 for lower $x$ values fall far too below, even those of the 300 K data (line 2), of the single crystals, and thus this phenomenon cannot be explained comprehensively by a simple local heating (or oxygenation) effect.

Possible origin(s) of the distortions in the present RS (with respect to bulk crystals) necessarily needs to be discussed, since this can be important in the understanding of the local structure of solution-deposited films and hint out the likely role of the material processing conditions.

In Fig. 7, and in the XRD experiments performed mainly on powder LM samples, it was observed that the material structure is “annealing atmosphere” dependent. A substantial incremental deviation from a nearly perfect oxygen stoichiometry may be the underlying factor behind the structural transition. By the refinement and literature match of the structure is “annealing atmosphere” dependent. A substantial the likely role of the material processing conditions. is mentioned, since this can be important in the understanding of the oxygen partial pressure has a critical role in determining the oxygen stoichiometry. Upon heating of the sample, and perhaps even lattice-matching substrates\textsuperscript{21}.

It is expected (and observed in many studies\textsuperscript{13,14,16,17}) that the sharp features in the RS of orthorhombic $\text{RMnO}_3$ crystals broaden and lose their intensity upon doping with alkaline-earth ($A$) elements. For example, the doping-related reduction in the JT disorder (stretching effect of the $\text{MnO}_6$ octahedra) is followed by the gradual disappearance of the Raman peaks in the high-frequency range, while only other spectral features in the low-frequency range remain [modes associated to bending and tilting behaviors of the $\text{MnO}_6$ octahedra and to relative movements of the $R(A)\text{−MnO}_6$ system], despite being subjected to some relatively minor changes. However, as discussed above, the present RS presented in Fig. 6 cannot be explained only by the disorder introduced via doping ($\text{Sr}$ for $La$), but also with the acceptance of the existence of some other kind(s) of disorder. Mainly a nonideal oxygen stoichiometry can be suggested as the main origin of disorder since the spectrum of the air-annealed LM film (Figs. 6 or 7), in fact, closely mimics those of oxygen-rich $La\text{−Mn−O}$ systems ($La\text{MnO}_{3+\delta}$), or, in other words, cation ($La$, $Mn$)-deficient $La_{1−\delta}\text{Mn}_{1−\delta}\text{O}_3$, reported previously.\textsuperscript{13,16,17} It would be reasonable to suggest that when the films are annealed in ambient air condition, it is expected that they reach the needed oxygen content with minimum difficulty, that is, towards $La(\text{Sr})\text{MnO}_3$. However, attainment of an ideal oxygen stoichiometry cannot be taken for granted under the present conditions.

Now we would like to discuss the possible origin of the $640 \text{ cm}^{-1}$ band in our doped films. In an earlier work on LSM powders, it was estimated via a simple chemical analysis method that as the amount of Sr increases the process of “sample oxygenation” slows down, and eventually comes to a stop, i.e., $\delta=0$, when $x=0.3$.\textsuperscript{20} It can be inferred from this finding that when the material crystallization is performed in an $O_2$-rich environment the regular doping and the “self-doping” effects become two competing processes, since both yield an increase in the Mn$^{4+}$ content. Nevertheless, since one can attribute the enlarged Raman peak widths in the present doped LSM films to the presence of excess oxygen, the band at $\sim 640 \text{ cm}^{-1}$ can also be attributed to this effect. However, this band starts to appear only after $x$ reaches 0.2, leaving also some other mechanism(s) as potential candidate(s) as for the origin(s) of this feature. In Fig. 6,
the films with $x=0$ and 0.1 have $d \approx 100$ nm while others are 300 nm thick. Therefore, an increase in the amount of (large) grains, with the increase of film thickness,\textsuperscript{21} can yield a larger surface area, which in turn, may enhance the oxidation of the $x=0.2$ and 0.3 samples. Dediu et al. reported the appearance and disappearance of a similar band in their thin LSM30 films, produced by a channel-spark method, after processing in oxygen or Ar ambient, respectively,\textsuperscript{15} when they are characterized with micro-Raman spectroscopy. These authors also reported a weakening or disappearance of this band, depending on the location of the microlaser probe; on the smooth parts (in some) of their films the signal was either weak or absent, in contrast with the strong scattering observable from/around of the some large (200 nm) “out-growth,” and assigned it to the presence of outgrowths, whereby considering them as (local) oxygen-rich regions. However, we believe that this is a more global phenomenon as for the present solution-deposited films. Finally, the evidenced polycrystallinity in our sol-gel films might play a partial role in the broadening of Raman bands, since this would also allow the breaking of the periodicity of a crystal system, resulting in a partial relaxation of the selection rules and by generating a long-range disorder.\textsuperscript{16,25} This effect is expected to be critically dependent on the size of the crystalline domains.

V. CONCLUSION

Microstructural characterization of solution-deposited polycrystalline La$_{(1-x)}$Sr$_x$MnO$_3$ and LaMnO$_3$ thin films was performed and the influence of the deposition parameters on their properties was demonstrated. The present results suggest the existence of some disorder, in the form of cation deficiency (due to excessive oxygen inclusion) and/or lack of infinite crystal order (as a result of polycrystallinity), present in sol-gel LSM films. The former could be attributed to annealing the films at ambient oxygen pressure, while it appears to be reasonable to suggest that the latter can be improved by obtaining films that are single crystalline and commensurate with substrate crystals.

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\textsuperscript{3}H. J. Hwang, A. Towata, and M. Awano, J. Am. Ceram. Soc. 84, 2323 (2001), and references therein.