Effects of thermal annealing on the texture of $La_{0.67}Sr_{0.33}MnO_3$ thin films

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Thin films of $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) were prepared at 670 °C on $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) substrates by liquid-delivery metalorganic chemical vapor deposition. X-ray diffraction analysis 2θ/θ and pole figure scans showed that the films are epitaxial with $(001)_{LSMO}//(001)_{LAO}$ and $(001)_{LSMO}//(001)_{STO}$. The crystal structure of LSMO/LAO was indexed as face-centered cubic with a double cell and LSMO/STO as simple cubic. Electron microscopy revealed square facets and elongated grain features. Films heat-treated between 700 and 800 °C on LAO resulted in a structural change, while those on STO showed an increase in texture.

$La_{0.67}Sr_{0.33}MnO_3$ (LSMO), famous for its impressive giant magnetoresistance (GMR) effect has been investigated due to its potential assistance in fuel cells, microelectromechanical system (MEMS) sensors, and other devices.[1–4] The influence of the microstructure on the properties of the LSMO epilayer (perovskite related structure) has been studied.[1,3] Deposition on different substrates such as $SrTiO_3$ (STO), MgO, and $LaAlO_3$ (LAO) results in different lattice mismatch at the film–substrate interface which affects strongly its properties.[5,6] Post annealed films of $La_{1-x}Ca_xMnO_3$ ($018 < x < 0.33$) has been found to be critical to the MR properties.[7] Here we report on the effects of thermal annealing on the texture of LSMO thin films deposited on LAO(001) and STO(001) single-crystal substrates.

The films were deposited by liquid-delivery metalorganic chemical vapor deposition method (LD-MOCVD). Details of the deposition procedures have been described elsewhere;[1,2] however, a brief description is given here. The reactor was operated under vacuum and heated to 670 °C with oxygen as the oxidant. The precursors were weighted and dissolved in diglyme with the help of a sonication. The solution was transported by argon to the reactor zone. The total pressure in the reactor was about 5 torr. The films were then heat-treated at 700 and 800 °C under argon/air (760 torr, 50% O_2) between 2 and 6 h. The phase analysis was checked by 2θ/θ scan using Cu K_α radiation. The in-plane texture was probed by pole figure through a series of ϕ scans. The films' topography was analyzed by scanning electron microscopy (SEM) (JEOL JSM-840, Tokyo, Japan). The LAO(001) and STO(001) substrates were purchased from MTI Co., Richmond, VA and used as received without any modifications.

The x-ray diffraction (XRD) 2θ/θ scan of the as-deposited thin LSMO films on LAO is shown on Fig. 1. The films were epitaxially grown with $(001)_{LSMO}//(001)_{LAO}$ and can be indexed as face-centered cubic (FCC) with a double cell lattice parameter. The XRD patterns revealed very small reflections at 32.45° and 58.45°, which correspond to (022) and (311), respectively. These reflections were not observed on the

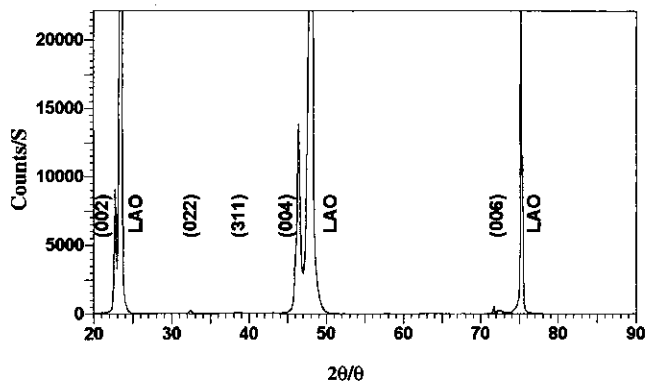

FIG. 1. XRD 2θ/θ scan of as-deposited thin films of LSMO/LAO heterostructure.

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substrate. The reflections at 72–73° are impurities from the LAO; however, the LSMO (006) reflection is also expected at that range. The lattice parameter perpendicular to the interface ($d_{\perp}$) using the (00l) reflection is 7.820 Å on the basis of the FCC double cell. However, at a film thickness of approximately 300 nm the strain was expected to be completely relieved;[1,3,4] thus, the lattice parameter was anticipated to be closer to the bulk value (3.873 Å). The c-axis elongation is characteristic of the compressive strain (2.1%) exerted by the substrate on the film. This distortion can also be attributed, in part, to the mismatch in the coefficient of thermal expansion between the film–substrate (Table I). For films annealed at 700 °C, the XRD pattern (not shown) revealed only a single reflection around $2\theta = 22°$. From this reflection alone it is difficult to discern the pattern, and the disappearance of the substrate peaks implies a change in the crystal structure.

The $2\theta/\theta$ scans of LSMO on STO are displayed on Fig. 2. The crystal structure is indexed as simple cubic (SC). For the as-deposited films (thickness approximately 250 nm), the c-axis lattice parameter could not be deduced because the film–substrate peaks overlapped. However, for the annealed films, the lattice parameter (3.891 Å) was determined after deconvoluting the (002) reflection. A value less than the bulk value were expected due to the tensile strain (approximately 1%) exerted by the substrate on the film. The distortion of the crystal structure in the c-axis direction is an interesting occurrence, and others have made similar observation.[8]

Figure 3 displays the (110) pole figures of LSMO on LAO and STO. Four reflections located at a tilting angle (Ψ) of 45° reveal the presence of the in-plane orientation with $(001)_{LSMO}//(001)_{Substrate}$. For the as-deposited LSMO on STO, it is difficult to know if the reflections are due to the films or to the substrate because their peaks are overlapped. However, we have observed an increase in crystallinity after annealing the films at 800 °C.

The elemental analysis was performed using energy dispersive x-ray spectroscopy (EDS), which shows a nominal composition of $La_{0.67}Sr_{0.33}MnO_3$ for all as-deposited films. SEM micrograph [Fig. 4(a)] shows that the as-deposited LSMO on LAO is smooth with only of

TABLE I. Properties of the as-deposited LSMO films: lattice plane, parameters, mismatch, and % strain. The lattice parameter for LSMO (bulk) = 3.873 Å; LAO = 3.821 Å, and STO = 3.900 Å. Coefficient of thermal expansion (CTE): LSMO = 13.4×10^{-6} K^{-1}, LAO = 1×10^{-6} K^{-1}, and STO = 10.30×10^{-6} K^{-1}.

Subs	Thickness (Å)	Lattice Structure	Lattice Parameters (Å)	Mismatch (%)	FWHM[a]
LSMO/LAO	3000	FCC	7.82	2.1	0.2
LSMO/STO[b]	2500	SC	3.891	1	0.3
LSMO (Powder)	···	SC	···	3.872	···

[a]Estimated from the 2θ peaks. [b]Annealed at 800 °C.

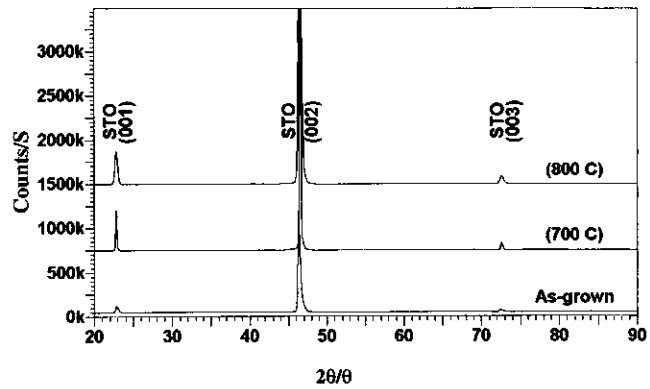


FIG. 2. XRD $2\theta/\theta$ scans of both as-deposited and annealed LSMO/STO heterostructure.

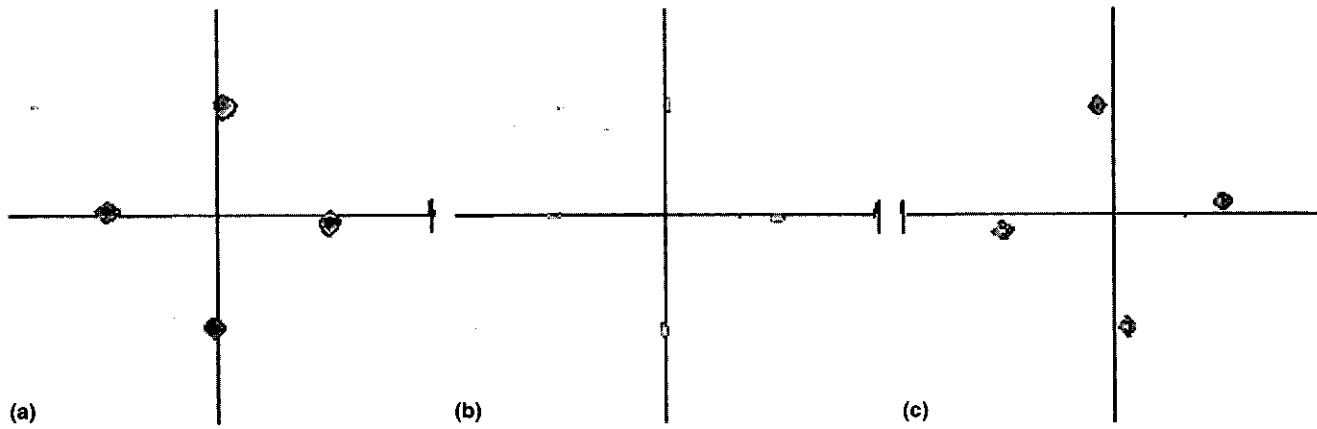
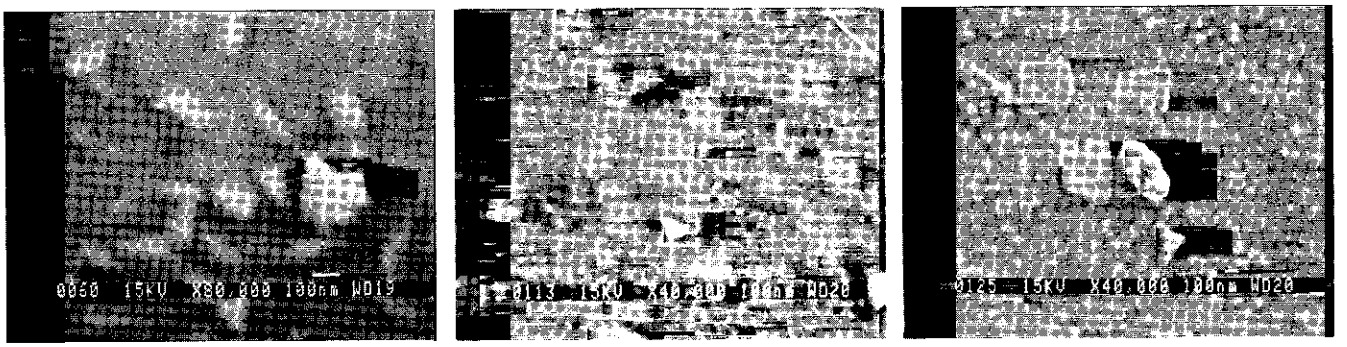


FIG. 3. X-ray diffraction pole figures of the (110) reflection, $2\theta = 32.76°$, of (a) as-deposited LSMO films on LAO, (b) as-deposited LSMO on STO, and (c) annealed LSMO on STO at 800 °C.



(a) (b) (c)

FIG. 4. SEM micrographs of LSMO/LAO (a) as-deposited and LSMO/STO (b) as-deposited and (c) heat-treated at 800 °C.

a few elongated grains. The annealed films (not shown) exhibited a change in color from black to gray. This is interesting because it implies that film deposited on LAO may be unstable after annealing under the aforementioned conditions. This has been corroborated by the XRD, which shows a change in crystal structure. Indeed, the structural compatibility of the LSMO/LAO composite may facilitate an interfacial reaction. In addition, atomic diffusion through the interface is also possible. It has been observed by others that the LSMO peaks on LAO disappeared after annealing up to 900 °C.[4]

The surface topography of both as-deposited and annealed LSMO on STO is shown on Figs. 4(b) and 4(c). A few large grains with a distinct square facet (250 × 250 nm) can be seen on the surface. Figure 4(c) shows evidence of an increase in crystallinity after annealing at 800 °C. The smaller grains become more noticeable; but overall, there are no structural changes. The interface between LSMO and STO is stable.[4]

In summary, this communication shows that the annealed films revealed an increase in texture and no change in crystal structure for the LSMO/STO sandwich. On the other hand, LSMO on LAO undergoes a structural change. We have shown that the surface morphology depends on the substrate and the heat treatment. These observations show the dependence of texture on both the substrate and the annealing temperature. It is important to note that we found no clear evidence of a change to polycrystalinity for the LSMO on STO.

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