Three-dimensional strain states and crystallographic domain structures of epitaxial colossal magnetoresistive La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin films

Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708

L. Wu and F. Tsui
Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27599

(Received 29 July 1998; accepted for publication 1 October 1998)

The evolution of three-dimensional strain states and crystallographic domain structures of epitaxial colossal magnetoresistive La$_{0.8}$Ca$_{0.2}$MnO$_3$ films have been studied as a function of film thickness and lattice mismatch with two types of (001) substrates, SrTiO$_3$ and LaAlO$_3$. In-plane and out-of-plane lattice parameters and strain states of the films were measured directly using normal and grazing incidence x-ray diffraction techniques. The unit cell volume of the films is not conserved, and it exhibits a substrate-dependent variation with film thickness. Films grown on SrTiO$_3$ substrates with thickness up to ~250 Å are strained coherently with a pure (001)$^T$ orientation normal to the surface. In contrast, films as thin as 100 Å grown on LaAlO$_3$ show partial relaxation with a (110)$^T$ texture. While thinner films have smoother surfaces and higher crystalline quality, strain relaxation in thicker films leads to mixed (001)$^T$ and (110)$^T$ textures, mosaic spread, and surface roughening. The magnetic and electrical transport properties, particularly Curie and peak resistivity temperatures, also show systematic variations with respect to film thickness.

Since the recent discovery of the colossal magnetoresistance (CMR) effect in epitaxial thin films of doped LaMnO$_3$, there has been renewed interest in these materials for device applications. The occurrence of CMR behavior has been attributed to the presence of lattice strain and disorder in epitaxial films. It has been shown that the CMR effect in epitaxial La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) films decreases with increasing film thickness and strain relaxation, confirming the important role of lattice strain. More recently, Suzuki et al., O’Donnell et al., and Kwon et al. have shown that strain also plays a dominant role in magnetic anisotropy of LCMO and La$_{0.75}$Sr$_{0.25}$MnO$_3$ (LSMO) films. Millis and co-workers have studied the effects of strain in LCMO films by measuring the out-of-plane lattice parameters and combining them with in-plane strains from calculations using Poisson’s ratio, and by assuming coherence in the growth plane for films thinner than 150 Å.

In order to study the structural dependence of magnetic and electrical transport properties of these films, it is essential to characterize the structures in terms of both in-plane and out-of-plane lattice parameters. Furthermore, the thin-film unit cell volume and its distortions may not be the same as those of the bulk. Volume expansion or contraction caused by epitaxy can be stabilized by partial cation substitution or oxygen nonstoichiometry. Films grown at low temperatures and low oxygen partial pressure are known to be more susceptible to substrate constraints.

In this letter, we report studies of the evolution of three-dimensional (3D) strain states, crystallographic domain structures, and magnetic and transport properties of epitaxial La$_{0.8}$Ca$_{0.2}$MnO$_3$ (LCMO) films as a function of film thickness and lattice mismatch with substrates. The bulk-doped manganite LCMO is a distorted perovskite with a pseudocubic lattice parameter ($a_0^P$) of 3.881 Å. The tilting of the MnO$_6$ octahedra results in a tetragonal structure with lattice parameters $a_0^T = b_0^T = 2a_0^P$ and $c_0^T = 2a_0^P$. In this work, Miller indices used for LCMO films are based on this tetragonal unit cell, indicated by a superscript "T". The tetragonal distortion enables one to distinguish between the (110)$^T$-oriented films, which are equivalent to (100) or (010) in the pseudocubic perovskite unit cell, and the (001)$^T$-oriented films, which are equivalent to (001) pseudocubic perovskite, by using off-axis azimuthal ($\phi$) x-ray scans, similar to what has been reported for epitaxial SrRuO$_3$ films. The ability to distinguish the two tetragonal orientations is crucial for studying magnetism in these films, particularly magnetic anisotropy.

The LCMO films were grown on (001) LaAlO$_3$ ($a_0 = 3.792$ Å) and (001) SrTiO$_3$ ($a_0 = 3.905$ Å) substrates using a pulsed laser ablation technique from a stoichiometric target. The two substrates were used to provide two different types of lattice mismatch for the growth of LCMO films, ~2.37% with LaAlO$_3$ (LAO) and ~+0.60% with SrTiO$_3$ (STO). The operating pressure was kept at 400 mTorr of oxygen with the substrate temperature held at 700 °C during deposition. The thickness of the films was varied from 100 to 4000 Å. Wavelength dispersive x-ray spectroscopy (WDS) confirmed that the composition of the films is the same as the target’s within experimental error.

The 3D strain states and lattice parameters were determined by normal $\theta$–2$\theta$ and grazing incidence x-ray diffraction (GID) $\theta$–2$\theta$ scans. For all the films studied, the only
intensities observed in the normal $\theta - 2\theta$ scans are from the substrate (001), and the film (001)$^T$ and/or (110)$^T$ reflections. We note here that GID is a surface sensitive technique, and that surface strain may not be the same as that of the bulk of the film.

The evolution of in-plane and out-of-plane lattice parameters, and the associated strains as a function of film thickness for the two different substrates are shown in Fig. 1. As expected, the observed lattice parameters for the thinnest films exhibit the largest deviations from those of the bulk, with the in-plane values at or near the substrates'. As film thickness increases, lattice relaxation takes place; both in-plane and out-of-plane lattice parameters tend to deviate away from those of the substrates towards the bulk value.

The bulk values were obtained from our x-ray measurements away from those of the substrates towards the bulk value.

The evolution of in-plane and out-of-plane lattice parameters and lattice strains of epitaxial LCMO films grown on $(001)$ LaAlO$_3$ and $(001)$ SrTiO$_3$ substrates. The lattice parameters of the bulk material measured from the target and of the substrate are indicated by the dashed lines.

FIG. 1. Film thickness dependence of the measured out-of-plane (triangles) and in-plane (circles) lattice parameters and lattice strains of epitaxial LCMO films grown on $(a)$ $(001)$ LaAlO$_3$ and $(b)$ $(001)$ SrTiO$_3$ substrates. The lattice parameters of the bulk material measured from the target and of the substrate are indicated by the dashed lines.

as a function of film thickness for films grown on the two substrates. For very thin films grown on STO, a pure $c$-axis texture was observed. The observed in-plane epitaxial arrangement is LCMO $[\bar{1}10]^T$ or $[\bar{1}10]_1||$STO $[100]$, and LCMO $[\bar{1}10]^T$ or $[110]_2||$STO [010]. Very thin films grown on LAO, on the other hand, exhibit a pure $(110)^T$ out-of-plane texture with two $90^\circ$ domains in plane, such that LCMO $[\bar{1}10]^T$ and $[001]^T||$LAO [100], and LCMO $[001]^T$ and $[\bar{1}10]^T||$LAO [010]. As film thickness increases, the pure domain structures are replaced by mixed ones, where both $(001)^T$ and $(110)^T$ textures co-exist, with the amount of mixture increasing with thickness (see Table I). This finding is consistent with previous transmission electron microscope observations. The observed strain states and domain structures, as shown in Table I, exhibit strong correlation between each other, indicating that they are linked directly. For instance, the observed strain sign change in films grown on LAO appears to coincide with the $50^\circ$ domain mixture, and the rapid in-plane lattice relaxation in films on STO seems to be associated with the initial appearance of $(110)^T$ textures.

Crystallographic quality of the films was analyzed using the measured full width at half maximum (FWHM) of the on-axis rocking curves. For the $250\,\text{Å}$ films, the rocking curve FWHM for the sample grown on STO is $0.25^\circ$, which is our instrument resolution, and it is between $0.25^\circ$ and $0.30^\circ$ for the sample on LAO, which is limited by the twinned structures of the substrate. As thickness increases, the rocking curves become broader, indicating an increased mosaic spread.

The zero temperature resistivity intercept ($\rho_0$) gives an indication of the disorder in the film.

In order to probe the strain relaxation processes in the films, evolution of crystallographic domain structures and textures were explored. Off-axis $\phi$ scans of nondegenerate reflections, such as $(111)^T$, $(113)^T$, and $(221)^T$, were used to identify the specific out-of-plane orientations. From the ratio of the integrated peak intensities between the $(001)^T$ and $(110)^T$ reflections ($I_{001}/I_{110}$), the amount of $(001)^T$ or $c$-axis domains in the film was determined, and the values are listed in Table I as a function of film thickness for films grown on the two substrates.

TABLE I. Measured structural, electrical transport and magnetic data and oxygen stoichiometry in the films.

<table>
<thead>
<tr>
<th>LaAlO$_3$ substrate</th>
<th>d (Å)</th>
<th>$I_{001}/I_{110}$ (%)</th>
<th>$T_p$ (K)</th>
<th>$T_e$ (K)</th>
<th>$\rho_0$ ((\mu\Omega,\text{cm}))</th>
<th>$\varepsilon_T$ (%)</th>
<th>$\varepsilon_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>68</td>
<td>258</td>
<td>244</td>
<td>472</td>
<td>$-0.38\pm0.11$</td>
<td>0.12±0.23</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>69</td>
<td>248</td>
<td>241</td>
<td>513</td>
<td>$-0.29\pm0.09$</td>
<td>0.04±0.23</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>58</td>
<td>241</td>
<td>222</td>
<td>520</td>
<td>$-0.20\pm0.07$</td>
<td>$-0.20\pm0.17$</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>43</td>
<td>240</td>
<td>225</td>
<td>484</td>
<td>$0.07\pm0.16$</td>
<td>0.21±0.35</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>35</td>
<td>236</td>
<td>223</td>
<td>686</td>
<td>$1.05\pm0.22$</td>
<td>$-0.06\pm0.53$</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>223</td>
<td>203</td>
<td>1005</td>
<td>$1.56\pm0.23$</td>
<td>$-1.06\pm0.54$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SrTiO$_3$ substrate</th>
<th>d (Å)</th>
<th>$I_{001}/I_{110}$ (%)</th>
<th>$T_p$ (K)</th>
<th>$T_e$ (K)</th>
<th>$\rho_0$ ((\mu\Omega,\text{cm}))</th>
<th>$\varepsilon_T$ (%)</th>
<th>$\varepsilon_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>68</td>
<td>230</td>
<td>215</td>
<td>591</td>
<td>$-0.45\pm0.03$</td>
<td>$-0.01\pm0.04$</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>76</td>
<td>212</td>
<td>201</td>
<td>605</td>
<td>$-0.32\pm0.11$</td>
<td>$-0.03\pm0.23$</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>76</td>
<td>207</td>
<td>194</td>
<td>819</td>
<td>$-0.53\pm0.03$</td>
<td>$-0.37\pm0.06$</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>77</td>
<td>205</td>
<td>198</td>
<td>878</td>
<td>$-0.53\pm0.11$</td>
<td>$-0.52\pm0.23$</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>87</td>
<td>202</td>
<td>188</td>
<td>1567</td>
<td>$-0.67\pm0.07$</td>
<td>$-0.39\pm0.17$</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>100</td>
<td>200</td>
<td>188</td>
<td>1731</td>
<td>$-1.16\pm0.11$</td>
<td>0.79±0.21</td>
<td></td>
</tr>
</tbody>
</table>
reduce electron–phonon interactions and increase the electron–phonon interactions and increase the electron–phonon interactions and increase the elec-

tronic hopping amplitude by decreasing the Mn–O bond length while increasing the Mn–O–Mn bond angle, all leading to a $T_c$ increase. In contrast, the Jahn–Teller distortion will lead to a localization of electrons and reduce $T_c$. However, the lack of correlation between the strain states and $T_c(T_p)$ shown here suggests that the transition temperatures are also influenced by other factors, such as inhomogeneities and disorder in the film.

In summary, we have studied the evolution of 3D strain states and crystallographic domain structures of epitaxial LCMO films as a function of film thickness and lattice mismatch. We show that observed strain states exhibit a systematic, substrate-dependent change with respect to film thickness, and that the unit cell volume is not conserved. While magnetic and transport transition temperatures also show strong film thickness dependence, they do not show correlation with strain states. Certain key questions, such as the origin of the observed domain structures, strain states at the growth temperature and at $T_c$, and all factors that control $T_c$ still need to be addressed, but the 3D strain states presented here give an important first step towards elucidating the magnetic and magnetotransport properties of CMR thin films.

This work was supported by the David and Lucile Packard Fellowship (CBE), the NSF Young Investigator Award (CBE), ONR Grant No. N00014-95-1-0513, and NSF Grant No. DMR 9802444. One of the authors (F.T.) acknowledges support from NSF Grant Nos. DMR 9703419 and DMR 9601825. The authors would like to thank Dr. Jonathan Sun for helpful discussions.