Epitaxial La_{0.7}Sr_{0.3}MnO_{3} thin films with two in-plane orientations on silicon substrates with yttria-stabilized zirconia and YBa_{2}Cu_{3}O_{7−δ} as buffer layers

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Epitaxial La_{0.7}Sr_{0.3}MnO_{3} (LSMO) thin films were fabricated on silicon substrates by pulsed laser deposition utilizing yttria-stabilized zirconia (YSZ) and YBa_{2}Cu_{3}O_{7−δ} (YBCO) films as buffer layers. Structural characterization showed that the epitaxial LSMO films were (001) oriented with two in-plane orientations and exhibited a columnar growth structure. In contrast, when LSMO was deposited directly on the YSZ/Si substrate without the YBCO template layer, it was characterized as a mixture of randomly oriented polycrystalline grains and (001)-oriented grains, without the columnar growth structure. The role of the YBCO layer for achieving the c-axis-oriented epitaxial LSMO film by introducing the dual-in-plane orientation mechanism on the YSZ/Si substrate has been analyzed. In addition, it was found that the LSMO film with the dual-in-plane orientations on the YBCO/YSZ/Si substrate exhibited a much lower resistivity compared to the LSMO film directly deposited on the YSZ/Si substrate. This effect is attributed to the existence of the randomly oriented grains in the latter, which resulted in more significant electron scattering at the grain boundaries. The higher density of grain boundaries in the LSMO film on YSZ/Si also led to a substantially higher magnetoresistance. © 2005 American Institute of Physics. [DOI: 10.1063/1.1876577]

INTRODUCTION

The perovskite La_{0.7}Sr_{0.3}MnO_{3} (LSMO) has potential use in various magnetic applications, such as magnetic-field sensors, hard disk read heads, infrared devices, and microwave active components, to name a few, due to its large colossal magnetoresistance (CMR). In addition, the high electrical conductivity of LSMO and its lattice matching with other perovskite ferroelectric oxides, such as lead zirconate titanate (PZT) and barium strontium titanate (BST), make LSMO an attractive candidate as the bottom electrode material for ferroelectric perovskite oxide thin films. As single-crystal materials often exhibit superior electrical and magnetic properties, epitaxial LSMO thin films are desirable for both electrical and magnetic applications.

Although epitaxial LSMO thin films can be grown on single-crystal oxide substrates with lattice-matching parameters, including SrTiO_{3} and LaAlO_{3}, reports of LSMO thin films grown on silicon substrates are very limited in the literature. There is no direct crystal lattice match between silicon and LSMO, and chemical reactions between LSMO and silicon could also occur to form interfacial phases. Thus, appropriate buffer layers need to be introduced in order to achieve high-quality epitaxial LSMO film growth. It is also of interest to investigate the epitaxial mechanism of LSMO film growth on buffer-layered silicon substrates to clarify how the structure develops and how the buffer layers affect the film properties.

In this paper, we describe the fabrication of LSMO films on an yttria-stabilized zirconia (YSZ) buffer layer on silicon. The YSZ layer has good lattice matching with the LSMO and prevents the formation of an interfacial layer between LSMO and silicon. By introducing an additional buffer layer of YBa_{2}Cu_{3}O_{7−δ} (YBCO) on the top of the YSZ layer, we can promote the epitaxial growth of (001)-oriented LSMO thin films. The epitaxial growth mechanism, crystal structures, surface morphology, resistivity, magnetoresistance, and the various interrelationships between these characteristics are discussed.

EXPERIMENTAL PROCEDURE

(100)-oriented silicon substrates were cleaned using nitric acid in an ultrasonic cleaner for 5 min to remove any natural oxide layer or oxide contaminant on the surface. The substrates were subsequently cleaned with de-ionized water, acetone, and ethanol. All the YSZ, YBCO, and LSMO thin films were prepared by the pulsed laser deposition (PLD) method, in which a KrF excimer laser was used (pulse duration 30 ns, wavelength 248 nm, Lambda Physik Lextra 200). The detailed processing parameters for all the three films are summarized in Table I. Two kinds of multilayer samples were prepared, namely, LSMO/YSZ/Si and LSMO/YBCO/YSZ/Si.
YSZ/Si. In addition, a LSMO film grown on a lattice-matching single-crystal LaAlO$_3$ (LAO) substrate was fabricated for comparison purposes.

Both θ-2θ and φ-scan x-ray diffraction (XRD, Bruker, D8-ADVANCE) studies were conducted to determine the crystalline phase and the crystal orientation of the films. Scanning electron microscopy (SEM, JEOL 6700F) was carried out to investigate the morphology of the films. A four-probe resistance measurement system (Keithley 220 current source, Keithley 182 voltmeter, and Lakeshore 330 temperature controller) was used to analyze the electrical properties of the samples from room temperature to 77 K. Magnetoresistance (MR) experiments with magnetic field up to 3000 G (homemade electromagnet) were also carried out at 77 K to assess the magnetic properties of the LSMO films.

**RESULTS**

**A. Crystalline structure**

XRD θ-2θ scans for the LSMO/YSZ/Si and LSMO/YBCO/YSZ/Si samples are shown in Fig. 1. An incomplete (001)-orientation preference and some unidentified phases are observed in the LSMO film grown on YSZ/Si, whereas the LSMO film grown on YBCO/YSZ/Si exhibits a complete (001) orientation and no unidentified phase is present. We did not observe strong XRD peaks of the YBCO layers because the power of the x ray was low (20 kV, 5 mA).

XRD φ scans for the LSMO/YBCO/YSZ/Si and LSMO/YSZ/Si samples are presented in Figs. 2(a) and 2(b), respectively. The YSZ layers exhibit a cube-on-cube epitaxial relationship to the (100)-oriented single-crystal silicon substrates for both samples, as revealed by the matched fourfold symmetry for both YSZ and silicon in Figs. 2(a) and 2(b). The LSMO film on the YSZ layer, which shows the incomplete (001) orientation in the θ-2θ scan in Fig. 1, exhibits a weak four-fold in-plane symmetry with broad diffraction peaks of plane [113], as shown in Fig. 2(b). From these results we can conclude that the LSMO film on the YSZ consists mostly of randomly oriented grains with a small number of epitaxial grains. For the LSMO/YBCO/YSZ/Si sample, the φ scan of the LSMO {103} plane exhibits strong eight-fold diffraction peaks, as shown in Fig. 2(a). This confirms that there are two

<table>
<thead>
<tr>
<th>Layer</th>
<th>Deposition temperature (°C)</th>
<th>Oxygen ambience (mbar)</th>
<th>Laser fluence (J/cm$^2$)</th>
<th>Repetition rate (Hz)</th>
<th>Deposition time (min)</th>
<th>Thickness ($\times$10$^{-9}$ m)</th>
</tr>
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<tr>
<td>YSZ</td>
<td>670</td>
<td>$5 \times 10^{-4}$</td>
<td>5</td>
<td>5</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>YBCO</td>
<td>650</td>
<td>$5 \times 10^{-3}$</td>
<td>3.5</td>
<td>3</td>
<td>8</td>
<td>200</td>
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<tr>
<td>LSMO</td>
<td>670</td>
<td>$2 \times 10^{-3}$</td>
<td>5</td>
<td>5</td>
<td>45</td>
<td>1000</td>
</tr>
</tbody>
</table>

**TABLE I. Summary of PLD processing parameters for the YSZ, YBCO, and LSMO thin films.**

![FIG. 1. X-ray diffraction patterns (θ-2θ) for the LSMO thin films deposited on YBCO/YSZ/Si and YSZ/Si substrates.](image1)

![FIG. 2. (a) X-ray diffraction patterns (φ scan) for (I) Si {113}, (II) YSZ {113}, and (III) LSMO {113} peaks for the LSMO/YBCO/YSZ/Si multilayer. The inset figure shows the relative φ angle relationship between YBCO {103} and LSMO {103}. (b) X-ray diffraction results (φ scan) for (I) Si {113}, (II) YSZ {113}, and (III) LSMO {113} peaks for the LSMO/YSZ/Si multilayer.](image2)
sets of in-plane orientations in the LSMO layer with an in-plane shift of 45° from each other. The two sets of in-plane orientation in the LSMO layer are found to result from the corresponding two sets of the in-plane orientation in the YBCO template layer, as indicated by the inset figure in Fig. 2(a). As Fig. 1 shows a complete (001) orientation, the LSMO film on the YBCO/YSZ/Si substrate is an epitaxial film but has two sets of in-plane orientation, with a shift of 45° from each other.

B. Morphology

SEM images of cross sections through the LSMO/YSZ/Si and LSMO/YSZ/Si multilayer structures are presented in Figs. 3(a) and 3(b), respectively. The LSMO film on the YSZ/Si substrate exhibits a columnar growth structure, as shown in Fig. 3(a), while the LSMO film grown on the YSZ/Si substrate does not show a columnar structure, as apparent from Fig. 3(b). The columnar grains in the LSMO film on the YBCO/YSZ/Si substrate are around 100–175 nm in width across the film. The LSMO film on the YSZ/Si substrate has more grain boundaries than the LSMO film on the YBCO/YSZ/Si substrate, which is also apparent from SEM images of the film surfaces (not shown). The SEM images indicate better epitaxial quality for the LSMO film on the YBCO/YSZ/Si substrate than that on the YSZ/Si, which is consistent with the XRD results. Both of the LSMO films show a root-mean-square surface roughness of around 10 nm by atomic force microscopy (AFM). Our LSMO films were always rather granular due to the nature of substantial structural mismatch and imperfect epitaxial growth by the pulsed laser deposition.

C. Resistivity and magnetoresistance

Figure 4 shows the temperature dependence of the LSMO film resistivity deposited on LAO, YBCO/YSZ/Si, and YSZ/Si substrates. The resistivity of the LSMO film on the YBCO/YSZ/Si substrate is much lower than that of the LSMO film on the YSZ/Si, which has randomly oriented grains, but is still higher than the resistivity of the epitaxial LSMO film grown on the lattice-matched substrate LAO.

The MR of the LSMO films deposited on YBCO/YSZ/Si and YSZ/Si substrates is given in Fig. 5. A magnetic field of up to 3000 G was applied perpendicular to the surface of the samples at 77 K. In Fig. 5, the LSMO film on the YSZ/Si substrate has much larger MR (~16%) than the LSMO film on the YBCO/YSZ/Si substrate (~2%). The results are consistent with the report by Gu et al. who found that LSMO films with a higher density of grain boundaries showed a larger MR.

DISCUSSION

The growth of YSZ on (100) silicon is based on a [100][100] cube-on-cube mechanism, which is the same as reported previously by our group. When the YBCO film was subsequently deposited onto the YSZ film, the YBCO film exhibited a strong c-axis orientation along the thickness direction and two in-plane orientations with a 45° shift from each other, i.e., YBCO[100][001]||YSZ[100][001] and YBCO[110][001]||YSZ[100][001], as indicated in Fig. 2(a). A similar dual-in-plane orientation for YBCO thin films was also reported in the literature. We also observed that the orientation of LSMO[100][001] is more preferred when the LSMO film is grown on the YBCO layer with the dual-in-plane orientation, i.e., YBCO[100][001]||YSZ[100][001] and YBCO[110][001]||YSZ[100][001], as its XRD intensity is much stronger than the orientation of LSMO[110][100] in Fig. 2(a). Without introducing the YBCO film, the LSMO on the YBCO/YSZ/Si substrate.
film on the YSZ did not exhibit the same in-plane orientation relationship with the underlying YSZ layer, as shown in Fig. 2(b). The epitaxial growth of YBCO[100][001]||YSZ[100] × (001) is obviously due to the small misfit of 6.24% for the (110) lattice of YBCO and (100) lattice of YSZ. However, it is interesting to note that YBCO[100][001]||YSZ[100][001] epitaxial growth occurred while LSMO, which apparently has similar lattice parameters, does not grow with the same in-plane orientation. The misfits for the YBCO/YSZ interface of the YSZ and YBCO, and provides more structural flexibility than LSMO. It is therefore essential to have the additional YBCO template layer in order to grow completely c-axis-oriented LSMO films through the dual-in-plane orientation mechanisms. With that being said, we do understand that there could be other oxide candidates to be used as a buffer layer instead of YBCO. However, our results show that the relatively complicated and more tolerant structure of YBCO may promote the epitaxial growth between two materials with substantial difference in structure, such as LSMO and YSZ described in this paper.

The difference in the resistivities of the LSMO/YBCO/YSZ/Si and LSMO/YSZ/Si films can be understood by consideration of electron polarization and scattering mechanisms. Inside the magnetic domain, the conduction electrons are spin polarized, i.e., having the same magnetic dipole direction, and electrons are easily transferred between pairs of Mn$^{3+}$ and Mn$^{4+}$ ions. However, when these electrons travel across the grain boundaries, they experience strong spin-dependent scattering. A large density of grain boundaries would lead to an increase in scattering and hence result in an increase of the resistivity. The lower resistivity of the LSMO film grown on YBCO/YSZ/Si as compared to the LSMO film on YSZ/Si is due to its complete $c$-axis orientation with the columnar grain structure. The smaller, randomly oriented grains in the LSMO/YSZ/Si form many more grain boundaries. It is therefore understandable that the LSMO films grown on YBCO/YSZ/Si show a larger resistivity when compared to the epitaxial LSMO film on LAO substrate, which has only one in-plane orientation.

With the application of a magnetic field, the randomly oriented magnetic domains in the LSMO film on the YSZ buffer layer are reoriented, which leads to a significant decrease in the resistivity. Therefore, a larger MR was observed in the LSMO film deposited on the YSZ/Si substrate than that on the YBCO/YSZ/Si substrate, which has no substantial amount of randomly oriented grains.

**CONCLUSION**

(001)-oriented epitaxial LSMO thin films with two in-plane orientations were fabricated on silicon substrates by
PLD with YSZ and YBCO films as buffer layers. The epitaxial LSMO films on the YBCO layers had a cross-sectional columnar growth structure. The dual-in-plane orientations of the LSMO film were formed by epitaxial growth from dual orientations in the YBCO template layer. The crystal orientation relationship among the LSMO, YBCO, and YSZ films can be expressed as, LSMO/YBCO[110][001]|YSZ[100]×(001) and LSMO/YBCO[100][001]|YSZ[100][001]. In contrast, when LSMO films were deposited directly on YSZ/Si without using the YBCO template layer, it contained a mixture of randomly oriented polycrystalline grains and (001)-oriented grains. Therefore, introduction of the YBCO layer was essential to obtain c-axis-oriented epitaxial LSMO films through the dual-in-plane orientation growth mechanism of YBCO on the YSZ/Si substrate. The difference between the in-plane orientations of the LSMO and YBCO films on the YSZ layer is mainly attributed to the disparity in their crystallographical structure. The LSMO film with the dual-in-plane orientations on the YBCO/YSZ/Si substrate exhibited a much lower resistivity as compared to the LSMO film on the YSZ/Si substrate, which had more randomly oriented grains and hence more electron scattering at the grain boundaries. The greater density of grain boundaries in the LSMO film on the YSZ/Si substrate also led to a substantially higher magnetoresistance.