Twinned LaAlO$_3$ substrate effect on epitaxially grown La–Ca–Mn–O thin film crystalline structure


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Abstract

La–Ca–Mn–O (LCMO) thin film was epitaxially grown on LaAlO$_3$ (1 0 0) substrate using RF magnetron sputtering. The epitaxial relationship between LCMO and LaAlO$_3$ (LAO), was characterized using MeV $^4$He$^2$ backscattering (BS)/channeling and a 4-circle X-ray diffractometer (XRD). The LCMO film deposited at 600°C with an RF power of 100 W showed the channeling minimum yield of 4.98% indicating its excellent crystallinity and high c-axis orientation. Through channeling angular scan measurement, it is confirmed that the 145 nm thick LCMO thin film conserved the compressive stress. The FWHM value of LCMO (2 0 0) peak in XRD $\theta$-rocking is mainly influenced by the twin structure of LAO substrate. It is also interesting that the twin angle of LAO substrate, 0.18°, is very close to the separation of two peaks, 0.20°, in XRD $\theta$-rocking scan on LCMO (2 0 0) peak. From these results, it is suggested that these two subpeaks in XRD $\theta$–2$\theta$ curve were originated from each twinned plane rather than coexistence of strained and relaxed layers. In addition, the FWHM of LCMO (2 0 0) peak obtained from high-resolution XRD $\theta$-rocking, 0.147°, is smaller than any value ever reported. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Since Jin et al. [1] reported the colossal magnetoresistance (CMR) from LCMO, one of the perovskite manganite materials, manganite thin films have been studied for high-density magnetic storage device and magnetic sensor applications. PLD [2,3], MBE [4,5], MOCVD [6], ion-beam sputtering [7], DC magnetron sputtering [8], RF magnetron sputtering [9], and sol–gel processing [10] have been used for the deposition of LCMO thin films. Jin et al. [11] also first reported the dependence of the CMR effect on film thickness,
and suggested that this phenomenon is caused by the stress between film and substrate. Afterwards, the dependence of CMR effect and film crystal structure changes on different substrates and film thickness has been investigated [12–14]. Among different single-crystal substrates for LCMO thin film deposition, LAO and SrTiO3 (STO) have been widely used due to their quite small lattice mismatch with LCMO. Recently, it was reported that 100 nm thick La0.6Sr0.4MnO3 on LAO (1 0 0) consisted of both relaxed and strained layers while 10 nm thick films have only strained layers [15]. In the case of LCMO thin films, the same phenomenon was observed when an LCMO thin film was post-annealed at 900°C for 4 h at the exposure of oxygen [16]. On the other hand, the LCMO thin films grown on STO (1 0 0) by ozone-assisted MBE [5] were observed to be fully strained and tetragonal up to at least 60 nm confirmed by X-ray diffraction (XRD) and RHEED. Such a fully strained epitaxial thin film was found even in LCMO/LAO [5], but its comprehensive structural characterization was not yet reported. Moreover, Rao et al. [17] suggested that the FWHM value of the LCMO films on LAO in the θ-rocking scan would be limited between 0.25° and 0.30° due to the twinned structure of LAO substrates, but they did not thoroughly investigate the effect of twinned LAO on the crystalline properties of LCMO films. In the present study, we report the effect of a twinned LAO substrate on an epitaxially grown LCMO thin film by RF magnetron sputtering.

2. Experimental procedure

LCMO thin films were deposited by RF magnetron sputtering using a La0.67Ca0.33MnO3 2" target, which was sintered from oxide powders prepared by sol–gel processing, on LAO (1 0 0) substrate. Prior to deposition, the substrate was cleaned using an ultrasonic cleaner in acetone and methanol for 5 min and then nitrogen was blown to remove residual solvent on substrate. The film was deposited at an RF power level of 100 W. The base pressure was 1 × 10⁻⁶ Torr and the working pressure was maintained at 50 mTorr, of which the partial pressure of Ar gas was 40 mTorr and that of O2 gas was 10 mTorr. The distance between target and substrate was 7 cm and the substrate temperature was fixed at 600°C using a halogen lamp heater. The deposited film was cooled in 1 atm pure O2 for 1 h after turning off the heater. The crystalline structure of the sputtered film and substrate was characterized by θ–2θ scan and θ-rocking using a 4-circle XRD. Backscattering (BS)/channeling was carried out to investigate the crystalline quality of the thin film. In addition, channeling analysis of the LCMO film on LAO through the ⟨0 0 1⟩ (crystal normal) and the ⟨0 1 1⟩ axial direction in the (1 0 0) plane was performed together to measure the strain of the LCMO thin film.

3. Results and discussion

Fig. 1 shows 2 MeV ⁴He²⁺ BS/channeling spectra of the LCMO film on a LAO substrate. The channeling minimum yield of LCMO film is 4.98% indicating the epitaxial growth of LCMO with good crystalline quality. The thickness and composition were estimated to be 145 nm and
La$_{0.8}$Ca$_{0.2}$MnO$_2$, respectively. From $360^\circ$ channeling polar scans (not shown here), it was observed that the film and substrate had the same $c$-axis. If misfit dislocation loops were formed at the interface to relieve the stress, a sudden increase of the channeling yield to the depth should be observed at the interface between film and substrate in BS/channeling spectra. However, it is not observed at the interface marked with dashed line. XRD $\theta$–$2\theta$ scan of the film (see Fig. 2) shows only \{h00\} family of planes of film and substrate indicating high $c$-axis orientation of LCMO film. The inset of Fig. 2 represents the enlarged XRD $\theta$–$2\theta$ feature of LCMO (200) peak which was clearly made up of two subpeaks separated by $\theta=0.31^\circ$. Li et al. [16] also observed these two subpeaks and explained that the left subpeak and the right one were related to strained layer due to tetragonal distortion and relaxed layer in LCMO/LAO.

In order to confirm the co-existence of strained and relaxed layers, channeling angular scans were performed. Fig. 3 shows channeling angular scans through (001) and (011) axial directions in the (100) plane for the LCMO film on LAO substrate. As shown in Fig. 3(a), there is no angle shift between LCMO and LAO channeling dip at the (001) normal incidence while the channeling dip of LCMO shifts 1.12$^\circ$ from that of LAO substrate at the (011) axial channel incidence. This implies that the film is elongated along only the $c$-axis direction due to compressive stress. In addition, only one channeling dip of the LCMO film in the (011) axial channel incidence indicates that the LCMO film is strained up to a thickness of 145 nm. If the LCMO films were partially relaxed to the pseudocubic phase, one more channeling dip at an angle of $0^\circ$ should be observed because in the case where the relaxed LCMO film and the LAO substrate have the same cubic structure, the

![Fig. 2. XRD $\theta$–$2\theta$ curve of LCMO thin film on LAO.](image1)

![Fig. 3. Channeling angular scans along (a) the (001) and (b) (011) channeling directions of LCMO and LAO.](image2)
(0 1 1) axial direction in the (1 0 0) plane for the pseudocubic LCMO film is the same as that for the cubic LAO substrate. This means that two subpeaks in XRD $\theta$–$2\theta$ scan do not come from strained and relaxed layers, respectively. Therefore, the $\theta$-rocking curves on LCMO film and LAO substrate were performed in order to investigate the origin of the two sub-peaks.

The rocking curves of the right subpeak on the LCMO (2 0 0) peak shown in the inset of Fig. 2 and of the LAO substrate without substrate rotation ($\phi = 0^\circ$) are shown in Figs. 4(a) and 5(a), respectively. As shown in Fig. 5 the XRD $\theta$-rocking curve of the LAO (2 0 0) peak shows two peaks sharply separated by as much as $0.18^\circ$ with an FWHM of $0.025^\circ$ and $0.007^\circ$, respectively. This means that the LAO substrate twin structure has a $0.18^\circ$ twin angle, which is consistent with the recently reported value for LAO substrates [18]. As shown in Fig. 4(a), it seems like the LCMO (2 0 0) peak consists of two subpeaks, even though these are not clearly resolved. It is very interesting that the separation of $0.20^\circ$ is very close to the $0.18^\circ$ twin angle of the substrate. This is also very similar to the calculated value of $\Delta \theta = 0.155^\circ$ from the two peaks in the inset of Fig. 2. Therefore, these two peaks in the XRD $\theta$–$2\theta$ curve appear to be generated not from strained and relaxed layers,
but films on each substrate twin plane. It is suggested from the above results that the twin structure of the LAO substrate served as a template for the LCMO thin film.

This twin structure is also observed as shown in Fig. 5(b) when the substrate is rotated by 90° ($\phi = 90^\circ$). Compared with XRD $\theta$–2$\theta$ results of the LCMO (2 0 0) peak shown in the inset of Fig. 2, the LCMO (2 0 0) peak from the XRD $\theta$–2$\theta$ scan at $\phi = 90^\circ$ does not split into two peaks (not shown here). The reason is that the 0.03° twin angle is too small to nucleate growth separately on each twin plane. Compared with Rao et al.'s result [17], a very small FWHM value of 0.147° in the rocking curve on LCMO (2 0 0) peak at $\phi = 90^\circ$ is observed in Fig. 4(b). This small value of FWHM is consistent with the 4.98% channeling minimum yield, indicating good crystalline quality of the LCMO thin film. This value is believed to be smaller than any other value ever reported.

The $c$-axis lattice constants of the cubic LAO substrate and LCMO film calculated from the XRD data in Fig. 2 are 0.3792 and 0.3987 nm, respectively. The former is exactly the same as the bulk LAO lattice constant and the latter calculated from the right peak is close to 0.3943 nm, calculated from the channeling dip angle difference, 1.12°, shown in Fig. 3. In this calculation, it is assumed that the $a$- and $b$-axis lattice constants of the LCMO thin film are equal to the $c$-axis lattice constant of the cubic LAO substrate, 0.3792 nm, which is based on the BS/channeling spectra results showing no misfit dislocation at interface. The exact crystalline structure and lattice constants of the bulk LCMO are not yet reported. Thus, in this paper, the pseudocubic structure, one of the widely used and accepted structures for the bulk LCMO in the calculation of lattice mismatch, is used. The reported pseudocubic lattice constant of LCMO bulk is in the range of 0.386–0.3881 nm [11,12,17]. Compared to lattice constants of LCMO bulk, the 145 nm thick LCMO thin film has compressive stresses and is elongated along the $c$-axis. From the above data, the magnitude of the compressive stress in the LCMO films is believed to lie in the same range as that of the theoretical case, 1.76–2.29%.

4. Conclusions

In summary, LCMO thin films were epitaxially grown on twinned LAO substrates by RF magnetron sputtering. In BS/channeling spectra the LCMO film on LAO was confirmed to be strained up to a thickness of 145 nm. The 0.2° spacing of the two subpeaks, which are not clearly resolved, in the XRD $\theta$-rocking for the LCMO (2 0 0) peaks was consistent with that of the 0.18° twin angle of the substrate. The twin structure of the LAO substrate served as a template for thin film growth, and affects the crystalline structure of the LCMO film.

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References