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2012

Cui, Y., Tian, Y., Shan, A., Chen, C., & Wang, R. (2012). Magnetic anisotropy and anomalous transitions in TbMnO₃ thin films. *Applied Physics Letters*, 101(12), 122406-.

<https://hdl.handle.net/10356/100676>

<https://doi.org/10.1063/1.4754544>

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Citation: [Applied Physics Letters](#) **101**, 122406 (2012); doi: 10.1063/1.4754544

View online: <http://dx.doi.org/10.1063/1.4754544>

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Magnetic anisotropy and anomalous transitions in TbMnO₃ thin films

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(Received 1 April 2012; accepted 7 September 2012; published online 19 September 2012)

TbMnO₃ thin films with different crystallographic orientations were deposited epitaxially on LaAlO₃ [100] and SrTiO₃ [100] single crystal substrates by using pulsed laser deposition. Magnetization measurements were performed along the [110], [−110], and [001] directions of the films. Obvious magnetic anisotropy and low temperature ferromagnetism were found. Transitions at $T \sim 10, 32, 120$, and 125 K along different directions are observed. The susceptibility anomalies, remarkably anisotropic, are discussed on the frame of the domain wall and strain-induced distortion. Particularly, the lattice mismatch and the anisotropic thermal expansion between the films and substrates are likely responsible for the distortion behaviors. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4754544>]

Upon the observations of the coexistence of ferromagnetic and ferroelectric polarizations as well as the coupling effect between them, multiferroic materials have attracted much attention for their fascinating properties and technological potential.^{1–3} Orthorhombic TbMnO₃ (TMO) is one of the few enumerable multiferroic materials where ferroelectricity arises from magnetic spiral order. Such characteristic is related to competing magnetic interactions at low temperatures eventually tuned by small lattice distortions, and with further consequences on the switchable electric polarization.^{4–10} Moreover, originating from the strain-induced deformation of the unit cell and subsequent unbalancing of magnetic interactions, intriguingly similar ferromagnetic properties have been reported in TMO films whereas its bulk counterpart is antiferromagnetic material.^{7–10} It was the early experimental observation of such effects in single crystal TMO that triggered intensive theoretical research and exploration of epitaxial thin films.³ To date, many efforts have been contributed to the preparations, characterizations, and properties studies of the TMO films.^{8–12} Most of the previous magnetic investigations are carried out with the magnetic field applied parallel to the sample surface. In fact, high quality TMO films have obvious crystallographic orientations. In this letter, we concentrate on the orientation-dependent magnetic anisotropy in the TMO films.

TMO thin films were fabricated on the LaAlO₃ (100) (LAO) and SrTiO₃ (100) (STO) single crystal substrates, as described in previous works.¹¹ Figs. 1(b) and 1(c) show the θ - 2θ scans of 40 nm thick films grown on LAO and STO and the insets show simple sketches of relative orientation between them. The TMO films are found to epitaxially grow with [110] direction perpendicular to LAO and c -axis oriented normal to STO, separately. As shown in Figs. 1(d) and 1(e), four narrow TMO (111) and (222) peaks were observed with an equal separation of 90°, accompanied by

four LAO (111) and STO (222) reflections located at 45° from the TMO (lll) peaks, separately. These results reveal that the TMO thin films are epitaxial orthorhombic. From the XRD patterns, the out-of-plane lattice parameters of the TMO films on LAO and STO are evaluated to be 0.786 nm and 0.741 nm, respectively. Compared with the bulk values of 0.788 nm and 0.740 nm, the TMO films were grown under tensile and compressive strained conditions on LAO and STO substrates, respectively, which is coincided with previous reports.^{6,7}

Magnetization measurements were performed using a superconducting quantum interference device (Quantum Design) along the [110], [−110], and [001] directions of the TMO films. [110] and [−110] are within the crystallographic ab -plane which is the magnetic easy plane and [001] is the magnetic hard axis.^{13–15} For the TMO film grown on LAO substrate, the magnetically hard c -axis is lying within the film plane together with [−110], whereas, [110] which is also within the ab -plane is perpendicular to the film or substrate. With this configuration, the crystallographic ab -plane is perpendicular to the substrate. For the TMO film grown on STO substrate, the [110] and [−110] directions are within the ab -plane in parallel to the substrate (inset of Fig. 2(d)).^{6,7} Fig. 2 shows the zero-field-cooling (ZFC) $M(T)$ measurements for the 40 nm TMO films grown on LAO and STO substrates, with the field of 200 Oe applied in parallel and perpendicular to the substrates.

Different levels of magnetization are recorded along the six different directions attributed to the presence of magnetic anisotropy, mainly the magnetocrystalline anisotropy and perhaps, the strain-induced anisotropy. The shape anisotropy of a magnetic thin film is characterized by the demagnetization factor ΔN with the expression, $\frac{1}{2}\mu_0 M_s^2 \Delta N = k_v$. Usually, ΔN is smaller than 0.1 for thin films, e.g., about 0.03 for Fe films^{16–20} or 0.05 for Co films.^{21,22} It is much larger for quasi-1D nanostructure such as Ni nanochains ~ 0.19 ,²³ nanowires ~ 0.20 ,²⁴ and Ni/Ni₂S₃ peapodlike chainstructures ~ 0.29 .²⁵ By adopting $\Delta N = 0.1$ for TbMnO₃ film, the shape anisotropy

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FIG. 1. (a) Perspective view of the distorted orthorhombic structure of TbMnO₃. (b) and (c) XRD patterns for the 40 nm TMO films on LAO and STO substrates, respectively. The insets show the schematic model of epitaxial relationship between the films and substrates, respectively. (d) ϕ -scan around LAO (111) and TMO (111) reflections. (e) ϕ -scan around STO (222) and TMO (222) reflections.

is about $K_v \sim 8.2 \times 10^5 \text{ erg/cm}^3$. For the estimation, the saturation magnetization, $M_s \sim 1140 \text{ emu/cm}^3$ ($\sim 150.6 \text{ emu/g}$) is adopted, which is the in-plane value taken along the a -axis of the single crystal,¹³ by using the theoretically calculated density, 7.57 g/cm^3 as the conversion factor. The shape anisotropy appears to be smaller than the magnetocrystalline anisotropy of single crystal, $K_1 = 5.77 \times 10^7 \text{ erg/cm}^3$,²⁶ by two orders of magnitude, and is therefore insignificant. The magnetocrystalline anisotropy is thus one of the dominant factors.

In Fig. 2(a), the ZFC $M(T)$ curve is for TMO grown on the LAO substrate, with the magnetocrystalline hard axis lying in the film plane. The field is applied normal to the film. The magnetization at temperature below 30 K is approximately the same for the out-of-plane component along the [110] as that for the in-plane components, as shown in Fig. 2(b), along the $[-110]$ and $[001]$ directions. Although the c -axis is the magnetocrystalline hard axis, the corresponding magnetization appears to be even slightly larger than that along the other directions, as revealed in

Fig. 2(b). Since the magnetic shape anisotropy is insignificant, there might be another factor favoring the magnetically easy orientation lying within the film plane. This could be due to the strain-induced anisotropy effect. For the TMO film grown on the STO substrate, on the other hand, the magnetocrystalline hard c -axis is normal to the substrate. Hence, the magnetization along the c -axis is much smaller than the in-plane component corresponding to the magnetocrystalline easy plane. The strain-induced effect might also favor the in-plane magnetization, making the difference between the in-plane and out-plane magnetizations even more pronounced, as presented in Figs. 2(c) and 2(d).

The magnetization curves in Fig. 2 show a sharp increase in magnetization with decreasing temperature at $T \sim 40 \text{ K}$. This is suggested as ferromagnetic-like.⁷ In particular, pronounced transition peaks at 10 K are also observed along the in-plane $[001]$ direction grown on LAO substrate (Fig. 2(b)), and along the out-plane $[001]$ direction grown on STO substrate (Fig. 2(c)). Since Tb³⁺ moments are located in the ab plane of a single crystal,^{13–15} the observed feature may be concomitant with the ordering of the Tb³⁺ moments in the strained films and the locking of Mn³⁺ ordering along the $[001]$ direction at low temperature.¹⁴ Interestingly, two different features are observed, one at 120 K on the $M(T)$ curve along the $[-110]$ direction (right inset of Fig. 2(b)) and the other at 125 K along the $[110]$ direction shown in Fig. 2(d). Although the difference between these two characteristic temperatures is not significantly large enough, these are of different origins and will be elaborated later.

The temperature dependent magnetization was measured by ZFC and field cooling (FC) conditions for the TMO film grown on LAO substrate. The field was applied in parallel to the film surface along the $[001]$ direction. Two sets of FC-ZFC $M(T)$ curves are obtained by two different measuring fields, 200 and 2000 Oe, and presented in Fig. 3. On the curves taken at 200 Oe, there is a ferromagnetic-like transition occurring at about $T \sim 30 \text{ K}$. This is consistent with the recent neutron diffraction results¹⁴ and can be assigned as the unlocking ordering of Mn moments in TMO. At 2000 Oe, the $M(T)$ curves are smooth, without any characteristic feature such as the lock-in transition or antiferromagnetic transition as reported previously for a TMO single crystal.³ This is likely attributed to the field-induced suppression of orderings of

FIG. 2. Temperature dependent magnetization under ZFC condition with a 200 Oe measurement field, perpendicular to (out-plane [110] (a) and parallel to (in-plane $[-110]$ and $[001]$ (b)) surface of TMO film on LAO substrate, perpendicular to (out-plane $[001]$ (c) and parallel to (in-plane $[-110]$ and $[110]$ (d)) surface of TMO film on STO substrate. Left and right insets of (b) are the second measurement $[001]$ $M(T)$ curve and the enlarged 120 K transition, separately. Inset of (c) is the enlarged 10 K transition. Inset of (d) is the coherence sketch of the domain of TMO film with STO substrate.

FIG. 3. Magnetization vs temperature plots of TMO film on LAO substrate measured along film [001] orientation under ZFC and FC conditions of 200 Oe and 2000 Oe, respectively. Inset is Magnetization versus magnetic field (H) at 5 K and the nested inset is the enlarged M-H.

Tb^{3+} and Mn^{3+} moments. The inset of Fig. 3 also shows $M(H)$ loops measured at 5 K. The coercivity is 550 Oe, which is shown in the nested inset of Fig. 3. It reveals the presence of a magnetic ordering phase at low temperature, supporting the observation by the $M(T)$ measurement.

For the TMO film grown on the STO substrate, the $M(H)$ loop measured at 5 K along the [110] direction is shown in Fig. 4(a). The coercivity is determined as 1050 Oe, better revealed in the inset. It indicates the presence of a magnetic ordering phase. This magnetic ordering phase is also revealed in the FC and ZFC $M(T)$ measurements with the strained TMO films at low temperature. Fig. 4(b) shows the FC and ZFC $M(T)$ measurements with the measuring field of 200 Oe in parallel to the film surface along the [110] direction. These curves exhibit a feature of antiferromagnetic-like transition at

FIG. 4. Magnetization measured on the TMO film grown on STO substrate, (a) Magnetization versus magnetic field (H) on [110] orientation at 5 K, and inset is the enlarged M-H. (b) Magnetization vs temperature plots on [110] orientation under ZFC and FC conditions of 200 Oe. (c) Magnetization vs temperature plots of TMO films with different thickness on STO substrates measured under ZFC condition with a 200 Oe measurement field along [110] direction. (d) Inverse susceptibility (χ^{-1}) as a function of temperature.

125 K, with only a barely recognizable kink on the FC branch. This feature also appears on the ZFC curves for the thicker films (150 nm and 180 nm) with the field of 200 Oe applied in parallel to the in-plane [110] direction (Fig. 4(c)). Interestingly, the magnetization curve along the $[-110]$ direction shown in Fig. 2(d) does not exhibit such a transition at ~ 125 K. It is more likely attributed to the spin reorientation ordering of Mn^{3+} along the [110] direction in the strained TMO film near 125 K instead of the phase transition of STO substrate at $T = 105$ K.²⁷

One further significant transition peak appears with the ZFC $M(T)$ curves at 32 K for the two thick films (150 and 180 nm in thickness) grown on the STO substrate, as shown in Fig. 4(c). For the thin film of 40 nm in thickness, however, a barely visible kink appears on the $M(T)$ curve at the same temperature. It indicates that this transition is sensitive to the substrate induced effect, and is almost washed out with the thin film of thickness as small as 40 nm. This is higher than the reported lock-in temperature, $T_L = 27$ K, but lower than the antiferromagnetic temperature at $T_N = 41$ K with a single crystal.³ Fig. 4(d) shows the inverse susceptibility versus temperature for the TMO film of 40 nm in thickness along the [110] direction. A change in slope is recognized at $T = 32$ K. The high-temperature linear section reveals a paramagnetic behavior at $T > 32$ K. Deviation from the linearity sets in, indicating a magnetic ordering transition occurs at low temperature with $T < 32$ K.

At room temperature, bulk TMO has an orthorhombic structure with parameters $a_f = 0.5294$ nm, $b_f = 0.5839$ nm, and $c_f = 0.7399$ nm, while LAO and STO substrates are cubic with $a_s = 0.3792$ nm and 0.3905 nm, respectively. For the TMO film grown on LAO substrate (inset of Figure 1(b)), the orientations between the film and the substrate are $\text{TMO}_{[001]}/\text{LAO}_{[100]}$ and $\text{TMO}_{[-110]}/\text{LAO}_{[010]}$. The lattice mismatches give rise to a tensile strain along the [001] direction and a compressive strain along the in-plane $[-110]$ direction for the film grown on LAO substrate. On the other hand, for TMO grown on the STO substrate, the ab plane of the TMO film is in parallel to the ab plane of the STO substrate with the relative orientations of the a -axis and b -axis with respect to the STO substrate as $\text{TMO}_{[010]}/\text{STO}_{[110]}$ and $\text{TMO}_{[100]}/\text{STO}_{[-110]}$, as shown in inset of Fig. 1(c). A slightly tensile strain and a highly compressive strain are along a_f and b_f directions for the film grown on STO substrate.⁷ With the thin films, there are four types of lattice matching for the TMO film lattice with the STO substrate.⁶ One can assume the TMO film [110] in parallel to the STO [010], then the film $[-110]$ deviates from the STO [100] as shown in the left inset of Fig. 2(d), and is elongated. Accordingly, the [110] experiences a compressive strain and the $[-110]$, a tensile strain.

Remarkably, epitaxial strain in orthorhombic YMnO_3 (YMO) thin films was found to induce Mn-O-Mn bonding angle modification which pushes the antiferromagnetic ground state from bulk E-type toward A-type across the region of cycloidal order.²⁸ Both TMO and YMO comprise very similar Mn-O-Mn geometry, the strain-induced changes may be similar in TMO films. Interesting transition structures with the $M(T)$ curves have been obtained along the directions experiencing compressive strain within the ab -plane of the TMO

FIG. 5. The cross-section bright-field TEM micrographs of the 40-nm-thick TMO films grown on LAO (a) and STO (b) substrates, respectively.

films. The one at $T = 120$ K is along the $[-110]$ direction of the TMO film grown on the LAO substrate, as shown in right inset of Fig. 2(b), whereas the other one at $T = 125$ K is along the $[110]$ directions of the TMO film on the STO substrates. The magnetization along the in-plane $[-110]$ direction is shown in Fig. 2(d). Perhaps, the anomalous transition like features observed on the $M(T)$ curves are associated with the moments of Mn^{3+} and Tb^{3+} in the ab plane, whose magnetic coupling strength is modified by the compressive strain.

Besides the lattices mismatch, the mismatch of thermal expansion coefficients between substrate and film also plays important roles, which can potentially leads to the temperature-sensitive physics properties, since the thermal expansion coefficients in the cubic STO and LAO are simply isotropic.²⁹ On the other hand, TMO single crystals show a strongly anisotropic thermal expansion: the thermal expansion coefficient is negative along the a axis, but positive along the b axis, and nearly zero along the c axis,³⁰ which increase remarkably with the temperature decreases especially in the range from 150 K to 100 K. These will initiate the displacements and rotations of ions in ab plane, then induce variations of the Mn-O-Mn bond angle, which is known to be the critical parameter for the magnetic properties.¹⁵

Moreover, Daumont *et al.* find orthorhombic crystallographic (antiferromagnetic) domains and the domain wall induced ferromagnetism in TMO films.⁶ In order to better understand the domains, the transmission electron microscopy (TEM) observations were performed using a JEOL 2100F electron microscope. Fig. 5 shows the cross-section bright-field TEM images of the 40-nm-thick TMO films grown on LAO and STO substrates, respectively. Both the images exhibit strained columnar domain structures, where the top of the columns is still relatively flat with unsharp column boundaries in the film grown on LAO substrate (Fig. 5(a)) and approaching a dome structure with relatively deep cusps at the column boundaries in which grown on STO substrate (Fig. 5(b)), separately. It is obvious that much more domain walls are in the TMO film grown on STO substrate than that on LAO substrate, which leads to the much higher coercivity in the former than that in the latter, as shown in the inset of Fig. 4(a) and the nested inset of Fig. 3. Though the high density of domain walls better explains the induced ferromagnetism observed in the TMO films at low temperature, which also leads to the decrease of in-plane anisotropy,⁶ a more complex analysis of the magnetic structure

of the TMO films is needed to explain the observed magnetic anisotropy and anomalous transitions.

In summary, the orientation-dependent magnetizations with the TMO films on LAO and STO substrates are investigated. Interesting anomalous transitions at ~ 120 K and 125 K are observed, which are likely attributed to the compressive strain within the ab plane. The peaks at $T = 32$ K on the $M(T)$ curves are sensitive to the film thickness, suggesting suppressed transition by lattice strain. The magnetization transition at $T = 10$ K could be related to the ordering of the Tb moments. Finally, TEM studies shed light on the strained columnar domains of the TMO films, which is believed to dictate the ferromagnetism properties.

We acknowledge the financial support from National Natural Science Foundation of China (No. 10975013).

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