LaMnO$_3$ Thin Films Grown by Using Pulsed Laser Deposition and Their Simple Recovery to a Stoichiometric Phase by Annealing

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We systematically investigated various physical properties of epitaxial LaMnO$_3$ thin films fabricated on SrTiO$_3$ substrate by using pulsed laser deposition. In particular, we observed drastic changes in their properties when the as-grown films were annealed in a reduced-oxygen atmosphere. Whereas the as-grown LaMnO$_3$ film showed ferromagnetic and semiconducting properties with a small optical band gap, the LaMnO$_3$ films annealed at temperature higher than 700 °C showed antiferromagnetic and insulating properties with an enlarged band gap. The optical features also changed drastically, in that the optical transition peak shifted to a higher energy with additional fine structures. Such changes were made in a direction such that the LaMnO$_3$ films were more stoichiometric, indicating that the stoichiometric phase could be recovered by simple annealing of the pulsed-laser-deposited films. Finally, possibilities of the polar catastrophe scenario at the interface between LaMnO$_3$ and SrTiO$_3$ are briefly discussed.

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I. INTRODUCTION

Perovskite transition-metal oxides are known for their rich physics originating from numerous degrees of freedom [1]. For example, LaMnO$_3$ (LMO) is a system whose lattice structure, charge dynamics, and magnetic and orbital ordering are strongly correlated to exhibit a variety of physical properties. Structurally, it undergoes a Jahn-Teller distortion at ~750 K and an orthorhombic-to-rhombohedral transition at ~1010 K [2, 3]. It also shows orbital ordering at ~750 K, which was recently described as an order-to-disorder transition related to the Jahn-Teller distortion [4,5]. Below the Néel temperature at ~140 K [6], LMO is an A-type antiferromagnetic (AFM) material. It is insulating at all temperatures, and has an optical band gap of ~1.7 eV [7, 8]. Moreover, LMO exhibits a colossal magnetoresistance or metallic behavior from various dopings [1,9]. It should be noted that LMO easily adopts excess oxygen or cation vacancies. In such cases, LMO usually becomes ferromagnetic and semiconducting [10–13]. Another example of a well-known transition-metal oxide is SrTiO$_3$ (STO). STO is one of the most widely used substrates for thin-film growth of another oxide. As a single crystal, it is a quantum paraelectric material with high dielectric constant at low temperature [14]. Contrary to LMO, STO easily adopts oxygen vacancies, and it becomes metallic and even superconducting at very low temperatures [15, 16].

Due to the rich physics of LMO regarding its lattice structure, it has often been deposited as a thin film form to investigate the strain effect. However when LMO is fabricated as thin films using techniques such as pulsed laser deposition (PLD), its tendency to attract oxygen often results in a non-stoichiometric phase [10–
Table 1. Summary of the structural, transport, magnetic, and optical properties of LaMnO$_3$ thin films for different annealing temperatures and times in a reduced-oxygen atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature ($^\circ$C)</th>
<th>Annealing time (h)</th>
<th>c-axis lattice constant (Å)</th>
<th>Conducting property</th>
<th>Activation energy $E_a$ (eV, from Arrhenius plot)</th>
<th>Magnetic property</th>
<th>Band gap $E_g$ (eV, from optical data)</th>
<th>Optical characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>As-grown</td>
<td>0</td>
<td>3.939 ± 0.02</td>
<td>semi-conducting low T</td>
<td>0.148</td>
<td>Ferromagnetic</td>
<td>0.33 ± 0.05</td>
<td>Red-shift of the d-d transition peak.</td>
</tr>
<tr>
<td>B</td>
<td>500</td>
<td>1</td>
<td>3.974 ± 0.02</td>
<td>insulating low T</td>
<td>0.190</td>
<td>Antiferromagnetic</td>
<td>0.55 ± 0.05</td>
<td>Clear three-peak structure observed as in stoichiometric LaMnO$_3$.</td>
</tr>
<tr>
<td>C</td>
<td>700</td>
<td>1</td>
<td>3.974 ± 0.02</td>
<td>semi-conducting high T</td>
<td>0.206</td>
<td>Antiferromagnetic</td>
<td>0.59 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>900</td>
<td>1</td>
<td>3.974 ± 0.02</td>
<td>semi-conducting</td>
<td>-</td>
<td>-</td>
<td>0.55 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>900</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

12. Especially, because STO tends to lose oxygen, a relatively high oxygen partial pressure is needed for the PLD growth of LMO on STO, which certainly modifies the stoichiometry.

Another important recent issue that can be addressed by studying LMO thin films on STO substrates is the polar catastrophe scenario at the LaMnO$_3$ (LAO) and STO interface [17]. When LAO is deposited on STO, the interface becomes highly conducting [18,19]. One of the proposed reasons for this conducting interface between two insulating oxides is the polar catastrophe scenario. Since LAO is an electrically polar material with alternating (LaO)$^{+1}$ and (AlO)$_2$$^{-1}$ layers, a polar discontinuous interface is formed when it is deposited on STO, which is a non-polar material with alternating (SrO)$^{0}$ and (TiO$_2$)$^{0}$ layers. Due to the polar discontinuity, an electric potential builds up with increasing polar layers and it is compensated by electric charges doped at the interface. However, there are other extrinsic possibilities that can explain the conducting behavior, such as oxygen vacancies or cation intermixing at the interface [20,21]. Since LMO has the same polar property as LAO with alternating (LaO)$^{+1}$ and (MnO$_2$)$^{-1}$ layers, studying LMO thin films on STO may provide insights to understand the interface between LAO and STO.

In this research, we investigated LMO thin films deposited on STO substrates by using pulsed laser deposition. By measuring their structural, transport, magnetic and optical properties, we observed that as-grown LMO films had ferromagnetic and semiconducting properties with a small optical band gap and c-axis lattice constant. After annealing in a reduced-oxygen atmosphere, we systematically observed that the films became antiferromagnetic insulators with enlarged optical band gaps and c-axis lattice constants. All of our experimental results consistently showed that the LMO film recovered its stoichiometric phase when annealed. An analogy to the interface between LAO and STO is also discussed in terms of the polar catastrophe scenario.

II. EXPERIMENTS

LMO thin films were fabricated using PLD on 0 0 1 STO single-crystal substrates with TiO$_2$ layer termination [22]. Both sides of the substrate were polished for the optical transmittance measurements. We used a 10-mTorr partial pressure of oxygen and a 700 °C heater temperature. The in-situ reflection high-energy electron diffraction intensity was observed to count the number of layers. The thicknesses of the samples were about 30 nm. To study the annealing effect, we used a gas mixture of 4% hydrogen and 96% argon. Table 1 shows the annealing conditions for different LMO thin films. We did not anneal sample A, but left it as a reference. Samples B, C, and D, were annealed at 500, 700, and 900 °C, respectively, for one hour. Sample E was annealed at 900 °C for three hours [10]. We also checked the effect of annealing on the STO substrate because in a reducing atmosphere, it might easily adopt oxygen vacancies. However, STO substrate remained insulating, and the optical transmittance property did not change at all upon annealing. This suggests that, despite the vacuum, the argon gas suppresses the escape of oxygen from the STO substrate.

We measured the structural, transport, magnetic and optical properties of the as-grown and the annealed LMO thin films. For structural and temperature-dependent transport ($\rho(T)$) properties, we used standard high-resolution X-ray diffraction (HRXRD) and four-probe measurements. The temperature- ($M(T)$) (zero-field cooled) and magnetic field- ($M(H)$) dependent magnetizations were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). We employed a normal-incident transmittance
geometry to measure the optical properties. A Fourier-transform infrared spectrometer (Bruker IFS66v/S) and a grating-type spectrophotometer (CARY 5G) were used to observe the spectral regions of 0.07 – 1.2 eV and 0.4 – 5.9 eV, respectively. We obtained optical absorptions by using the simple relation $\alpha(\omega) = \log \text{Tr}(\omega) - \log \text{Tr}_{\text{sub}}(\omega) / d_f$, where $\alpha(\omega)$ is the optical absorption, $\text{Tr}(\omega)$ is the transmittance of the LMO thin film on the STO, $\text{Tr}_{\text{sub}}(\omega)$ is the transmittance of the STO substrate and $d_f$ is the thickness of the film [23].

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD $\theta$ - $2\theta$ scans for the LMO thin films on STO substrates annealed at various conditions. The LMO 0 0 2 peak is observed near the prominent STO 0 0 2 peak, as indicated with arrows. The $\theta$ - $2\theta$ scans of the LMO thin films could be classified into two groups. When the annealing temperature was not high enough (500 °C, sample B), the sample showed a structure similar to that of the as-grown LMO (sample A). The LMO peak was just below the substrate peak and could not be well separated. When the annealing temperature was sufficiently high (more than 700 °C, samples C, D, and E), the LMO peak shifted to a lower degree and became distinct. We could calculate the out-of-plane lattice constants from the peak position; it increased from 3.939 ± 0.02 to 3.974 ± 0.02 Å upon annealing. Since the in-plane lattice constants were well strained to the substrate, such an increase in the out-of-plane lattice constants results in an increased unit cell volume.

Figure 2 shows an Arrhenius plot of the temperature-dependent resistivity curves for LaMnO$_3$ thin films annealed under different conditions. The films become more insulating with annealing.

C), it showed an insulating behavior with a two orders of magnitude decrease in the conductivity. The film became more insulating when the annealing temperature was 900 °C; the conductivity decreased about two orders of magnitude more. It should be noted that for samples A and B, there is a cusp at ∼170 K. This cusp is related to the magnetic ordering in the LMO thin films, which will be discussed in the next paragraph. We could fit the curves with the Arrhenius exponential function $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$, where $\sigma_0$ is a pre-exponential factor including the charge carrier density and mobility, $E_a$ is the activation energy and $k_B$ is the Boltzmann constant. From the slope of the curves in Fig. 2, $E_a$ values could be obtained and are summarized in Table 1. The $E_a$ values increased with increasing annealing temperature. We also note that for samples A and B, the $E_a$ values are larger at high temperatures than at low temperatures. We assume that the $E_a$ values are lower at low temperatures due to an enhancement of the double exchange mechanism of ferromagnetically-aligned spins.

To understand the origin of the cusp in the transport measurement for samples A and B, we measured the magnetization ($M$) of the LMO thin films. Figure 3(a) shows the temperature-dependent $M$ measured at 3 kOe. Samples A and B show a typical ferromagnetic behavior at temperatures below ∼170 K, with a saturated magnetization reaching ∼3.5 $\mu_B$/Mn at 10 K. On the contrary, samples C, D, and E show just a slight upturn of $M$ at temperatures below ∼145 K, with a saturated magnetization of ∼0.5 $\mu_B$/Mn. Figure 3(b) shows the magnetic-field-dependent $M$ at 10 K. Samples A and B again show a clear ferromagnetic hysteresis loop with a remnant magnetization of ∼2.2 $\mu_B$/Mn and coercive field of ∼0.6 kOe. However, when the LMO thin films were sufficiently annealed, the remnant magnetization decreased to ∼0.3 $\mu_B$/Mn. A slight increase of $M$ for sufficiently-annealed LMO samples, samples B, C, and D, is usually observed in bulk antiferromagnetic LMO, and
the canting of the antiferromagnetically-aligned spins is suggested as the origin. In addition, the antiferromagnetic ordering temperatures of samples B, C, and D are similar to those for bulk stoichiometric LMO at \( \sim 140 K \) [13]. Our results indicate that the ferromagnetic ordering for as-grown LMO is changed to antiferromagnetic ordering by annealing at a reducing atmosphere.

Figure 4(a) shows the optical \( \text{Tr}(\omega) \) for LMO thin films on STO substrates. The \( \text{Tr}(\omega) \) of bare STO substrates are also included for comparison. The similar \( \text{Tr}(\omega) \) for as-purchased and annealed STO substrates indicate that the physical properties of STO substrates are not influenced by annealing in a reducing atmosphere. The optical properties are also drastically different between samples A and B and samples C, D, and E. To analyze the spectra in more detail, we calculated the optical absorption spectra \( \alpha(\omega) \). Reliable \( \alpha(\omega) \) could be obtained in the transparent region of the substrate, i.e., up to 3.2 eV.

The calculated \( \alpha(\omega) \) is shown in Fig. 4(b). First, we note that the optical band gap, \( E_g \), of the as-grown LMO thin film (\( \sim 0.33 \text{ eV} \)) is enlarged for the sufficiently-annealed samples (\( \sim 0.55 \text{ eV} \)). \( E_g \) was estimated by the grey lines indicated in Fig. 4(b). This trend in \( E_g \) is the same as the trend in \( E_a \), which explains the decreased dc conductivity for the sufficiently-annealed LMO samples. Second, the peak corresponding to the \( d-d \) transition also shifts drastically from \( \sim 1.7 \text{ eV} \) for the as-grown sample to \( \sim 2.3 \text{ eV} \) for the sufficiently-annealed samples [8,24]. Third, additional optical absorption peaks appear below and above the \( \sim 2.3 \text{ eV} \) peak for the sufficiently-annealed LMO thin films. This three-peak structure is typical for the stoichiometric LMO [25, 26], although the origin is not yet very clear.

The structural, transport, magnetic and optical measurements of the systematically-annealed LMO thin films all point to the same conclusion. The LMO thin films annealed at more than 700 \( ^\circ \text{C} \) have recovered the properties of stoichiometric LMO whereas the as-grown and the insufficiently-annealed LMO thin films have different properties. This result indicates that a recovery to a stoichiometric LMO phase is possible by simple annealing. We now elucidate the reason for the different physical properties in the as-grown and the insufficiently-annealed LMO thin films. The main cause of the difference is thought to be the cation vacancies or excess oxygen [10,27]. LMO single crystals have been reported
to have smaller out-of-plane lattice constants when there are cation vacancies [28,29], as in our XRD experiment. Such cation vacancies, furthermore, result in a valence change of Mn ions, and Mn$^{3+}$ is introduced to LMO instead of Mn$^{3+}$. The Mn$^{4+}$ ions induce a double exchange between neighboring Mn$^{3+}$ ions, eventually resulting in ferromagnetically-aligned spins [13]. In addition, the double exchange mechanism enables the hopping of charge carriers, which will enhance the dc conductivity and reduce $E_g$. Finally, Mn$^{4+}$ ions will influence the optical spectral features. When Mn$^{4+}$ is doped to stoichiometric LMO, the three-peak structure usually disappears, and the peak shifts systematically to lower energy with increased doping [25]. The $\alpha(\omega)$ of our LMO thin films clearly demonstrates such behavior.

The tendency of LMO to have cation vacancies, or in other words, the tendency of Mn$^{3+}$ to become Mn$^{4+}$ prevents us from directly comparing the LMO/STO to the LAO/STO system. Opposite to Al ions, which do not allow valence state other than Al$^{3+}$, Mn ions can simultaneously have Mn$^{3+}$ and Mn$^{4+}$ valence states. This multivalence nature causes LMO to easily become a non-polar material by itself, so in this case, the polar catastrophe scenario cannot be properly applied. However, since LMO attracts oxygen more than LAO, the STO substrate adjacent to the LMO film should have oxygen vacancies at least as much as in the LAO/STO case. This might suggest that oxygen vacancies are not the main cause of the conducting interface in LAO/STO. A similar analogy can also be applied to cation intermixing. Since the SrO/TiO$_2$/La interface should be fabricated for both LAO/STO and LMO/STO heterostructures, the creation of (La,Sr)TiO$_3$ might not be the main origin of the conduction. At this point, however, we cannot rule out possibilities that might localize the charge carriers specifically in LMO/STO interface. One such possibility that should be considered is the presence of a magnetic moment in LMO. The correlation between the spin alignment in LMO and the charge carriers that might be induced will be a subject for further investigation.

IV. CONCLUSION

In conclusion, we investigated the structural, transport, magnetic and optical properties of epitaxial LaMnO$_3$ thin films. Due to the ability of LaMnO$_3$ to adopt excess oxygen and create cation vacancies, the as-grown films showed ferromagnetic and semiconducting behavior as for electron-doped, non-stoichiometric LaMnO$_3$. By systematically annealing in a reduced-oxygen atmosphere, we found that by simple annealing at a temperature higher than 700 °C, the antiferromagnetic and insulating phase of stoichiometric LaMnO$_3$ could be recovered.

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REFERENCES