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The influence of substrate orientation and annealing condition on the properties of $LaMnO_3$ thin films grown by polymer-assisted deposition

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ABSTRACT

The epitaxial films of $LaMnO_3$ were fabricated via a simple polymer-assisted deposition method. The effects of substrate orientation and annealing condition on the structure and properties of $LaMnO_3$ films have been investigated. It is found by X-ray diffraction and Raman spectroscopy that increase in the oxygen content results in a decrease in unit cell volume along with a reduction in Jahn–Teller distortion. Besides, with increase in annealing temperature, the resistivity of the film decreases and the insulator–metal transition temperature T_{IM} shifts to higher temperature. The maximum of the resistivity is highly substrate-orientation dependent in the ascending order of (1 0 0)<(1 1 0)< (1 1 1). Furthermore, the T_{IM} of $LaMnO_3$ film increases with the substrate orientation changing from (1 1 1) to (1 0 0). It is shown that magnetic order correlates well with an insulator to metal behavior. All results reveal that the lattice distortion of MnO_6 octahedron can be tuned by different annealing condition and the substrate orientation, which can be effective methods to adjust the structure, electrical and magnetic properties of $LaMnO_3$ films.

1. Introduction

In $LaMnO_3$ (Mn^{3+}, $t_{2g}^3e_g^1$ 3d configuration) [1], as a Mott insulator, like many insulator–metal transition oxides, the electrical properties are dominated by electron–electron interactions leading to a localization of the e_g conduction electrons. For a perfect stoichiometric $LaMnO_3$ (LMO), the magnetic ground states are expected to be A-type antiferromagnetic (A-AFM) [1]. However, LMO thin films grown on $SrTiO_3$ (STO) substrates have been experimentally found to be ferromagnetic (FM) [2]. The discrepancy could be traced back by considering lattice distortions in real manganites, which could severely be affected by extrinsic effects such as slight deviation from the chemical composition [3,4], oxygen content [5], and strain state [6–9] in real thin-film system.

The excess (deficit) oxygen can introduce Mn^{4+} (Mn^{2+}) ions along with Mn^{3+} ions in the system. It is well known that the presence of Mn^{4+} (Mn^{2+}) is associated with the change in distortion of oxygen octahedral leading to structural modification. Moreover, Mn^{4+} (Mn^{2+})–Mn^{3+} double exchange interaction drives the system into ferromagnetic and metallic states. It is reported that the different oxygen content of LMO bulk can be obtained by annealing conditions (annealing process and annealing atmosphere) [10,11]. Besides, the investigations on $La_{0.67}Ca_{0.33}MnO_3$ [12], $Sm_{0.5}Ca_{0.5}MnO_3$ [13], and $Bi_{0.4}Ca_{0.6}MnO_3$ [14] have demonstrated that the substrate orientation is another factor to induce anisotropic strain in manganites film. However, there are few reports about the effects of annealing condition and the orientation of the substrate on the property of LMO thin films, which are two effective ways to tune the lattice distortion of manganite films. The aim of this work is to figure out the effects of the annealing condition and the substrate orientation on the electronic transport property of LMO thin films.

2. Experimental

LMO thin films were fabricated by polymer-assisted deposition (PAD) technique, which shows favorable features compared to the traditionally used vacuum techniques, including a low investment cost, fast deposition with high yield, and most importantly it is an easily scalable and continuous process [15–17]. In order to obtain the LMO films, the necessary precursor solution was prepared as follows. First high-purity (>99.99%) metal salts $La(NO_3)_3{\cdot}nH_2O$

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(0.5 mmol) and $Mn(NO_3)_2$ (0.5 mmol, AR, 50 wt% in H_2O) were dissolved in deionized water with 0.2922 g of ethylene diamine tetraacetic acid (EDTA) and 0.2922 g of polyethylenimine (PEI; 1:1 mass ratio to EDTA) with a molecular weight of 70,000. The mixed solution was stirred by a magnetic stirring apparatus for 10 h at room temperature and then kept being stirred in a 60 °C oil-bath until the solution remaining ~5 mL. To obtain the LMO polymeric films, the stable precursor solution was coated on pre-treatment (1 0 0)-, (1 1 0)-, and (1 1 1)-oriented $SrTiO_3$ (STO) and (1 0 0)-oriented $LaAlO_3$ (LAO) substrates with 5000 rpm (revolutions per minute) for 40 s by the dip-coating method. Such a technique allowed us to obtain epitaxial thin films effectively. The thickness of the film can be easily controlled by the concentration of precursor and the coating speed. According to the thermal decomposition analysis of PEI, the coated polymeric films were heated up in a muffle furnace in different atmospheres. A low ramp rate of 0.5 °C min^{-1} was used from room temperature to 700 °C in order to make sure that the water evaporated and PEI burned up to avoid the formation of bubbles on the film surface. The samples were then ramped (at the rate of 5 °C min^{-1}) to annealing temperature. After 2 h heat treatment, the films were slowly cooled down to room temperature with a rate of 1 °C min^{-1}.

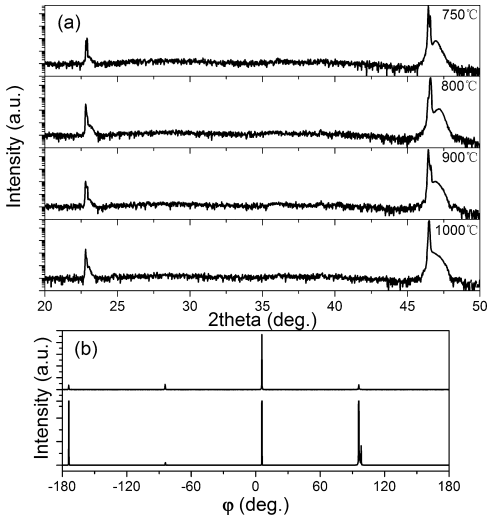

Fig. 1. (a) XRD $\theta/2\theta$ symmetric scan for LMO epitaxial thin films grown on (1 0 0) STO at different annealing temperature; (b) φ scan of the (1 0 1) reflections of the LMO thin film annealed at 900 °C (top) and the STO substrate (bottom).

3. Results and discussion

The X-ray diffraction (XRD) patterns of LMO films grown on (1 0 0) STO annealed at 750, 800, 900, and 1000 °C in air, respectively, are shown in Fig. 1a, in which only the (0 0 *l*) peaks for both the film and the substrate can be found, indicating the preferential *c*-axis orientation of the thin film along with the (0 0 *l*) substrate crystallographic direction. No secondary phase is detectable. The in-plane φ scan (asymmetric Bragg reflection) for (1 0 1) reflection of the LMO thin film annealed at 900 °C as well as that of the STO substrate is shown in Fig. 1b. The φ scans of LMO films grown on STO reveal that the films are of good epitaxial quality. Moreover, the epitaxial relationship between the LMO films and the (1 0 0) STO substrate is confirmed to be (0 0 1) LMO//(0 0 1) STO and (1 0 0) LMO//(1 0 0) STO, which indicates that the LMO films grown on substrate as a "cube-on-cube" mode [18]. Besides, the surface morphology characteristics of LMO grown on STO with different annealing temperature were detected by SEM as shown in Fig. 2, which reveal that the LMO film becomes denser, less grain boundary by increasing the annealing temperature. In order to further confirm the thickness for LMO film with high accuracy, the X-ray reflectivity for LMO/STO was taken as shown in Fig. 3, from which the thickness of LMO/STO annealed at 900 °C is obtained to be about 40 nm. The results of XRD and SEM indicate that the PAD is a simple and effective method to obtain epitaxial perovskite film.

The temperature-dependent resistivity of the LMO film grown on (1 0 0) STO annealed at different temperature is shown in Fig. 4. It can be found that the electronic transport properties of LMO/STO show large variations in the resistivity and insulator–metal transition temperature (T_{IM}) with increasing annealing temperature. The T_{IM} shifts to a higher temperature and the resistivity decreases with increasing annealing temperature, which may be ascribed to the following points: (a) the better crystallinity and surface morphology. With increasing annealing temperature, the denser and less grain boundary for films is

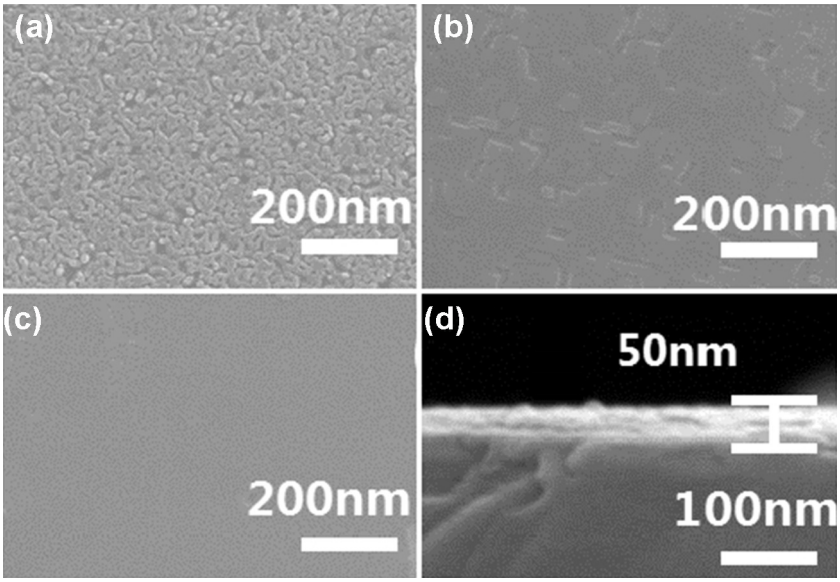

Fig. 2. The SEM micrographs of the LMO/STO epitaxial thin films annealed at different temperatures: the surface morphologies of the LMO films annealed at (a) 750 °C, (b) 800 °C, and (c) 900 °C, respectively; (d) the typical cross-sectional area of LMO film annealed at 900 °C.