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Annealing Effect on Transport and Magnetic Properties of $La_{0.67}Sr_{0.33}MnO_3$ Thin Films Grown on Glass Substrates by RF Magnetron Sputtering

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The manganite $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films were grown on glass substrates in a mixed argon and oxygen atmosphere by using RF magnetron sputtering. The structural characteristics, transport behaviors and magnetic properties of LSMO films were studied by annealing the films in air at 550 and 620°C. The out-of-plane lattice parameter $a_{\rm LSMO}$ contracted after annealing and was close to that of bulk LSMO $a_{\rm bulk}$, indicating that the internal strain was fully relaxed. Nanocrystalline grains were observed in the annealed films. Enhanced saturation magnetization and metal-to-insulator transition temperature ($T_{\rm MI}$=268 K) were also obtained. Curie temperatures ($T_{\rm c}$) of the as-grown films was 340 K with the same as that of annealed at 550°C, but dropped to 315 K when the annealing temperature increased to 620°C, which can be attributed to the oxygen release during annealing in atmosphere.

KEY WORDS: $La_{0.67}Sr_{0.33}MnO_3$; Annealing; Magnetron sputtering; Nanocrystalline

1. Introduction

Doped perovskite manganites $La_{1-x}Sr_xMnO_3$ (LSMO) have been studied for over 50 years due to their unique ferromagnetic and electronic characteristics[1], such as the high degree of spin polarization of the carriers at the Fermi level, colossal magnetoresistance (CMR), and Curie temperature ($T_{\rm c}$) in excess of room temperature[2]. Many experimental methods, for instance, pulsed laser deposition (PLD)[2], magnetron sputtering[3,4], metal organic chemical vapor deposition (MOCVD)[5], and polymer-assisted deposition technique[6,7], have been used to prepare LSMO films. Among these techniques, sputtering is a promising method for depositing LSMO thin films because of its low cost, heat cycling and ability to grow films at low temperature with good properties. In addition, sputtering has a relatively high deposition rate and is well suited to industrial-scale large area deposition[8]. However, as a result of many factors, such as defects, oxygen deficit, lattice strain, and grain boundary, LSMO films deposited by sputtering always exhibit different properties from bulk materials. Many attempts have been made to improve the quality of LSMO films by means of varying substrate, sputtering pressure, and annealing temperature[9–12]. Single-crystal substrates, such as $LaAlO_3$ and $SrTiO_3$, because of the small degree of lattice mismatch, are always used to prepare high quality LSMO films[2,3,12]. However, expensive cost makes them unsuitable for broad range of application. In this paper, LSMO films were grown on glass substrates by RF magnetron sputtering from a LSMO stoichiometric ceramic target in a mixed argon and oxygen atmosphere. The annealing effect on the magnetic and electrical transport properties of LSMO films is investigated.

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2. Experimental

The LSMO films were deposited on cover glass (corning) substrates (22.5 mm × 30 mm) by RF (13.56 MHz) magnetron sputtering from a LSMO stoichiometric ceramic target (6 cm diameter). Prior to deposition, the substrates were cleaned ultrasonically and degreased in acetone. A base pressure of less than 3×10^{-4} Pa was established, then the substrates were heated to 400°C. The sputtering was carried out in a mixed atmosphere of 40% argon and 60% oxygen. Sputtering pressure and RF power were maintained at 1.0 Pa and 100 W, respectively. Sputtering procedure was maintained for 40 min. The film thickness was 340 nm in average for all the samples, which was confirmed by thickness profilometer. After deposition, samples were cooled down to room temperature and introduced to an annealing furnace. As the glass substrates were distorted at high temperature 650°C, the films were annealed at 550 and 620°C for 30 min in the atmosphere, respectively.

The structural characteristics were analyzed by using a Rigaku D/MAX-rA X-ray diffractometer (Japan) using a Cu*Kα* radiation. The surface morphologies were analyzed by using a JEOL JSM-7600F scanning electron microscope (Japan). The electrical transport properties were measured through four-terminal configuration. The magnetic properties were measured by superconducting quantum interference device (SQUID) with the magnetic field parallel to the film surface.

3. Results and Discussion

3.1 Annealing effect on the properties of lattice structure

The X-ray diffraction (XRD) patterns of as-grown and annealed films deposited on glass substrates are shown in Fig. 1. The patterns can be indexed by a rhombohedral lattice with space group $R\bar{3}C$. All the films show (012), (110), and (024) peaks, which indicates the polycrystalline structure. After the LSMO films are annealed at 620°C for 30 min in the atmosphere, the diffraction intensity increases and the full width at half maximum (FWHM) decreases, proving that the annealing procedure results in a better crystalline. All the peaks have a slight shift towards higher 2θ angle after annealing, which may be related to the strain change in the films. The (110) peak becomes dominating in the XRD patterns of the annealed films. The crystallite size along this plane in the film annealed at 620°C is about 17 nm evaluated by Scherrer formula[13], which is larger than that of the as-grown film. After annealing at 620°C, an out-of-plane lattice parameter contraction is detected in the films. The out-of-plane lattice parameter $a_{\rm LSMO}$ decreases from 0.396 nm in the as-grown films to 0.388 nm in the annealed films. The latter is close to the pseudocubic lattice parameter of bulk LSMO materials ($a_{\rm bulk}$, ~0.389 nm)[2], implying that the strain is relaxed through the annealing procedure. As mentioned above, the films annealed at 650°C are distorted macroscopically. The distortion to some extent also exists in the films annealed at lower temperature, though it cannot be seen macroscopically. Corning glass is a mixture of SiO_2 (major component), B_2O_3 and Al_2O_3, and their lattice parameters are all smaller than that of LSMO. Moreover, corning glass is amorphous. Hence, compressive strain exists inevitably in the films due to the lattice mismatch between the substrate and the LSMO. As a result, the in-plane lattice contracts and the out of plane lattice parameter a_{LSMO} is stretched. During the annealing procedure, the substrate goes soft to a certain extent and the atoms at the interface get more energy to relax. The strain built in the film gets released after annealing and a coherent interface is formed[14]. As a result, the out-of-plane lattice parameter $a_{\rm LSMO}$ decreases closely to a_{bulk}.

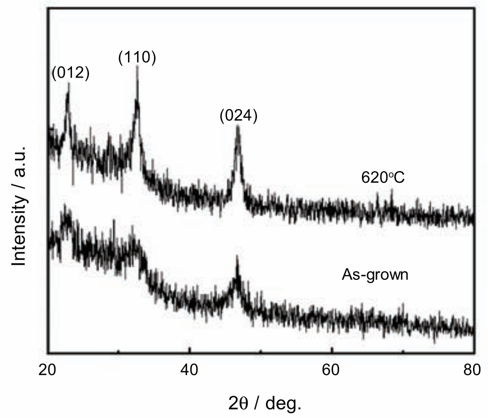

Fig. 1 XRD patterns of as-grown and 620°C annealed LSMO films on glass substrates. The patterns are not corrected for glass substrates

3.2 Annealing effect on the surface properties of LSMO films

The surface morphologies of the films are investigated by scanning electron microscopy (SEM). Figure 2 shows the surface micrographs of as-grown film and 620°C annealed film. It can be seen that the surface of as-grown films is relatively smooth. Some black shallow holes can be found distributing randomly in the surface. After annealing, white crystal grains can be clearly found, especially in the areas near the shallow holes, showing that the grains become larger during annealing. The observed changes in grain sizes are consistent well with that of XRD measurements.

3.3 Annealing effect on the transport properties of LSMO films

The temperature-dependent resistances of the as-

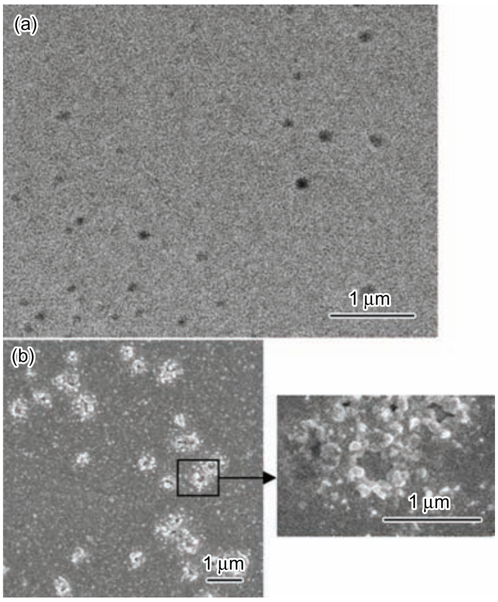

Fig. 2 SEM images of LSMO films on glass substrates: (a) as-grown, (b) annealed at 620°C

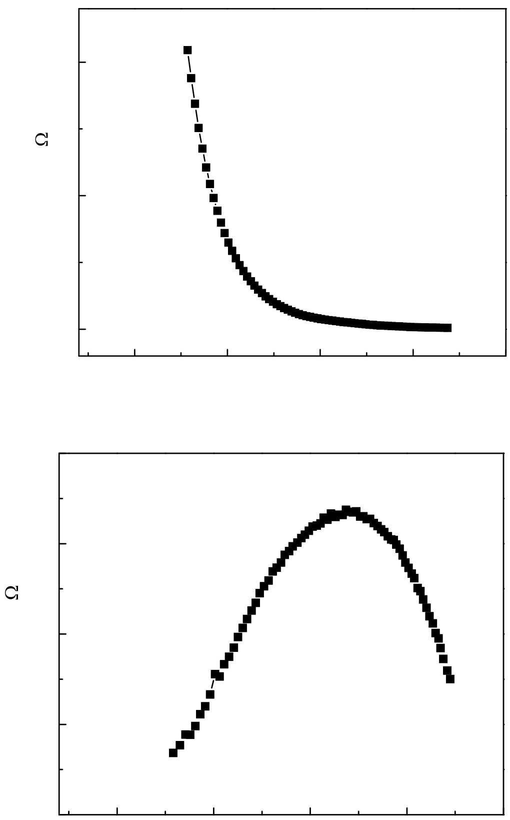

Fig. 3 Temperature dependence of resistance: (a) as-grown films, (b) films annealed at 620°C

grown LSMO films and annealed films are shown in Fig. 3. In manganite LSMO films, there exists an interplay between ferromagnetic double exchange (FM-DE) interaction and antiferromagnetic superexchange (AFM-SE) interaction[15], which results in a metal-to-insulator phase separation. Nevertheless, this phenomenon does not exist in our as-grown films. As shown in Fig. 3(a), an insulator-like behavior is presented when the temperature decreases from 320 K. The insulating behavior is mainly due to the grain boundary scattering effect which always exists in the polycrystalline manganite films[16]. A clear metal-to-insulator transition is observed after the films are annealed at 620°C. It presents a phase transition from FM/metal to AFM/insulator at transition temperature T_{MI} (Fig. 3(b)). This may be caused by the relaxed compressive strain in the annealed films. The compressive strain can decrease the Mn-O-Mn bond length and bond angle, which may significantly weaken the double exchange interaction[17]. Accordingly, the annealing eliminates the strain and enhances the FM double-exchange interaction. The resistance peak occurs at T_{MI}=268 K, which is lower than T_{c} (obtained from our magnetic measurement). This is attributed to the particle size effect[18].

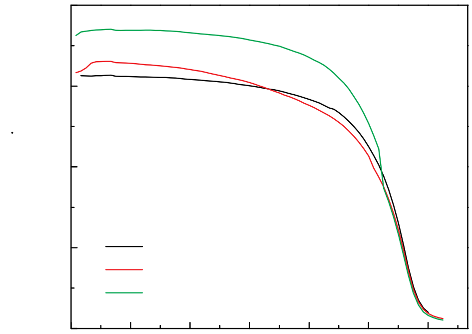

Fig. 4 Temperature dependence of zero field-cooled (ZFC) magnetization behavior of the as-grown films and films annealed at 550 and 620°C

Furthermore, the resistance of the films decreases several orders of magnitude over a large temperature range after annealing. It stems from the decrease of grain boundary by annealing procedure. The connectivity between grain boundaries is enhanced by the annealing[16]. All this leads to a remarkable reduction of resistance in the annealed films. Note that, in our previous experiments, the resistance of films annealed at 650°C (the glass substrate is distorted) is about 300 Ω at room temperature, about three orders of magnitude smaller than that of the as-grown films.

3.4 Annealing effect on the magnetic properties of LSMO films

Figure 4 demonstrates the temperature dependence of zero field-cooled (ZFC) magnetization behavior of the as-grown and 550, 620°C annealed films. The magnetic field of 1000 Oe is applied parallel to the film surface in all samples. The ferromagnetic transition temperature T_{c} defined as the temperature of the maximum slope in dM/dT, is measured to be 340 K in

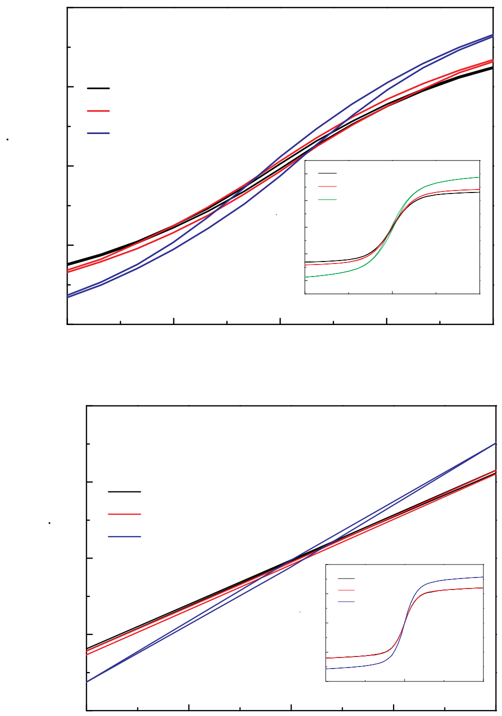

Fig. 5 Magnetic hysteresis curves of different samples: (a) measured at 20 K, (b) measured at 300 K

as-grown films. For 550°C annealed films, T_c is almost unchanged. However, it decreases to 315 K when annealing temperature reaches to 620°C. This phenomenon can be attributed to an oxygen content reduction under annealing in atmosphere. As the LSMO films are prepared in excess oxygen atmosphere, the oxygen in the films is released during annealing in the atmosphere. The oxygen release leads to the T_c reduction.

The magnetic hysteresis curve is presented in Fig. 5. All the samples measured at 20 and 300 K show typical ferromagnetic characteristics. The coercivity is measured to be about 64 Oe in 620°C films at 20 K (Fig. 5(a)), larger than that of as-grown films (24 Oe) and 550°C films (45 Oe). The reason can be also related to the defect caused by oxygen release in the annealing procedure. The coercivity in all samples is decreased to several Oe at 300 K (Fig. 5(b)). Furthermore, enhanced saturation magnetization is found with the increased annealing temperature, which may be induced by strain relaxation and the particle size effect. The long-range ferromagnetic order suffers severe degradation as the particle sizes decrease[18], and larger grains lead to enhanced ferromagnetic order, thus, easily magnetized. The magnetization is enhanced remarkably when the films are annealed at 620°C. The saturation magnetization of 620°C annealed films is about 670 emu/cm^3 at 300 K, which is approximate to that of bulk materials.

4. Conclusion

In summary, LSMO films were prepared on glass substrates successfully by RF sputtering method. The structural characteristics, transport behaviors and magnetic properties of LSMO films were investigated by annealing the samples in atmosphere at 550 and 620°C. The 620°C samples showed better crystalline quality, the maximum saturation magnetization and metal-to-insulator transition temperature T_{MI} (268 K). The highest T_c (340 K) was achieved in the as-grown films and the 550°C annealed films.

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