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Characterization of epitaxial LSMO thin films with high Curie temperature prepared on different substrates

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ABSTRACT

We investigated structural, electrical and magnetic properties of epitaxial $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films (20–100 nm thick) deposited by pulsed laser ablation on different substrates. Single crystalline substrates: (001) $SrTiO_3$, (001) $LaAlO_3$, (001) $La_{0.26}Sr_{0.76}Al_{0.61}Ta_{0.37}O_3$ and (001) MgO were used to vary the substrate-induced epitaxial strain. The LSMO films exhibit very good crystal quality and enhanced temperatures of metal-insulator transition (T_{MI}) as well as temperature of ferromagnetic ordering (Curie temperature, T_C) up to 451 K with $T_{MI} = T_C$ coincidence of both temperatures. The enhanced T_C (T_{MI}) values were analyzed with respect to substrate-induced strain and LSMO film thickness. We ascribe the increased T_C (T_{MI}) values to decreasing strength of electron-phonon coupling coming from Jahn-Teller splitting. The substrate-induced strain in the LSMO films only decreased the T_C (T_{MI}) values depending on magnitude of biaxial strain.

1. Introduction

Electrical, magnetotransport as well as structural properties in manganite epitaxial thin films have been studied intensively for many years. The possibility to control the electrical and magnetic properties of manganite films by induced strain has been presented by many authors [1–10]. The commonly applied method for experimental study of epitaxial strain effect is the growth of these films on single-crystalline substrates with a certain lattice mismatch. When the film is grown on a substrate with smaller (larger) lattice parameter than that of the bulk manganite material the epitaxial strain is expected to be compressive (tensile). However, the coherently strained state can be kept only to some thickness ranging from about 12 nm [11] to 100 nm [2,6] when the epitaxial strain starts to relax and the manganite film recovers its bulk properties. Millis et al. [12] suggest two sources of strain dependence: a uniform compression with tendency to increase the electron hopping and biaxial strain which increases the Jahn-Teller (JT) splitting with tendency to localize the electrons. Both effects influence the temperature of ferromagnetic–paramagnetic transition T_C (Curie temperature – the temperature above which the material loses its ferromagnetic ordering and becomes paramagnetic) as well as the metal-insulator transition temperature T_{MI} (at which the resistivity presents its maximum); and these temperatures correlate in manganites [13]. Studies [14,15] revealed that compressive strain is an effective tool to enhanced T_C (T_{MI}), however, biaxial distortion leads to reduction of T_C (T_{MI}) [7].

In this work we investigate structural, magnetic and electrical properties of epitaxial $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) thin films deposited by pulsed laser deposition. The films were grown on single-crystalline substrates (001) $LaAlO_3$ (LAO), (001) $SrTiO_3$ (STO), (001) $La_{0.26}Sr_{0.76}Al_{0.61}Ta_{0.37}O_3$ (LSAT) and (001) MgO to vary the substrate-induced epitaxial strain. Despite the various induced epitaxial strain in the LSMO films the metal-insulator transition temperatures reported by us are significantly higher than those reported by others [1–10]. The purpose of this article is to reveal the origin of increased values of T_C and T_{MI} utilizing the model presented in Ref. [12]. The structural, electrical and magnetotransport properties of the LSMO films with enhanced T_C (T_{MI}) above bulk LSMO values (~370 K) were described elsewhere in our previous works [16–19]. The hopping regime in electrical transport properties of the LSMO thin films with enhanced T_C (T_{MI}) values was also studied and we found out that a small polaron hopping transport mechanism described well our experimental resistivity data [20].

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2. Experimental details

The LSMO films were deposited onto a one-side polished (001) oriented single crystalline STO, LAO, LSAT and MgO substrates using pulsed laser deposition (PLD) system (MBE/PLD-2000). A KrF excimer laser operating at 248 nm with a pulse width of 20 ns, repetition rate of 10 Hz and energy density of 6 J/cm^2 (spot size on the target ~2 mm^2) was used to grow the LSMO films. The temperature of the substrate holder was kept to 850 °C and the oxygen pressure was set to 53 Pa during the deposition. After the deposition, the films were cooled down at a rate of 20 °C/min in O_2 (4×10^4 Pa). The thickness of the LSMO films varied between 20 and 100 nm. The growth rate of the LSMO was 6.5 nm/min.

A Bruker D8 DISCOVER diffractometer equipped with X-ray tube with rotating Cu anode operating at 12 kW was used to determine the crystallographic orientation perpendicular to the film surface (θ-2θ configuration). To determine the in-plane orientation of the LSMO films with respect to the major axes of the substrates, ϕ-scans were carried out. The lattice parameter values of the LSMO films were determined from linear "l" and "h" scan measurements.

The temperature dependence of the resistivity was measured using a standard dc four-probe technique in a temperature range of 4–480 K. The magnetic properties of the films were measured at temperatures ranging from 10 to 500 K, using a SQUID magnetometer (MPMS-XL7) and a vibrating sample magnetometer (PPMS-9T), all from Quantum Design. The magnetization vs. temperature (M(T)) measurements were performed in the field of 5 mT applied in the film plane.

3. Results and discussion

LSMO films were grown on STO, LAO, LSAT and MgO to induce various biaxial strains. The bulk manganite LSMO can be described as a slightly deformed pseudocubic perovskite lattice with a lattice parameter $a_{bulk} = 0.3876$ nm and a unit cell angle 90.26°. The lattice mismatches between the bulk LSMO and the substrates are LAO (−2.14%), STO (0.75%) and LSAT (−0.2%) so they can induce biaxial compressive, tensile and little strain in LSMO films, respectively. In spite of this large mismatch between the LSMO and the MgO (8%) the LSMO films exhibit epitaxial and relaxed growth [17,19].

The composition (stoichiometry) of the films was verified by Auger spectroscopy or Rutherford backscattering spectrometry as presented in our previous works [16,19]. The average cation composition ratio La:Sr:Mn of all films well corresponds to the target composition (La:Sr:Mn = 0.67:0.33:1).

The prepared LSMO films exhibited very good crystal quality. Fig. 1 shows examples of X-ray diffraction (XRD) investigations of the LSMO film grown on the STO substrate: (a) θ-2θ scan, (b) φ-scan, (c) linear "h" scan and (d) linear "l" scan. In the θ-2θ scan only LSMO 00*l* were present, indicating the absence of any spurious phase. To determine the in-plane growth properties, ϕ-scans of the LSMO (204) and substrate (204) planes were carried out. We observed four sharp maxima indicating the four-fold symmetry of the LSMO lattice. Our XRD analyses confirmed that the LSMO grew epitaxially on the LAO, STO, LAT and MgO substrates. The in-plane $a_{||}$ and out–of plane $a_{\perp}$ lattice parameters of the LSMO films are estimated from "h" and "l" linear scans. Fig. 1d shows that in-plane lattice parameter of the LSMO film is identical to the substrate (STO), but the out–of plane lattice parameter of the LSMO film is smaller than the STO substrate (Fig. 1c, $a_{\perp} = a_{\perp sub} \times l_{sub}/l$, $a_{\perp sub} = 0.3905$ nm, $l_{sub} = 4$, $l = 4.057$). The in-plane and out–of plane lattice parameters of 50 nm thick LSMO films grown on different substrates are summarized in Table 1.

Recently, we have shown that in epitaxial LSMO films deposited on MgO, there is a correlation between electrical and magnetic properties described by the double exchange (DE) theory [13,17]. Moreover, the Curie temperature and the metal insulator transition temperature coincide. Similar experiments confirm the coincidence of electrical and magnetic properties ($T_{MI} = T_C$) also for the LSMO films grown on other substrates presented here. An example of such coincidence is shown in Fig. 2a, b for the LSMO on LSAT where the temperature dependence of reciprocal LSMO magnetization and temperature dependence of LSMO resistivity are plotted. The beginning of the ferromagnetic transition well corresponds to temperature of resistivity maximum at 430 K (inset in Fig. 2a). The corresponding resistivity maxima are $\rho_{MI} = 6$, 5, 3.5 and 4.5 mΩcm for LSMO on LAO, STO, LSAT and MgO substrates, respectively. The T_C (T_{MI}) values are significantly higher than reported previously (320–390 K) [1,2,5,6,10]. Therefore, it is interesting to find out whether such an increase of T_C (T_{MI}) can be caused by substrate induced epitaxial strain.

The strains in the LSMO films are expressed as $\varepsilon_{||} = (a_{||} - a_{bulk})/a_{bulk}$ for in-plane strain and $\varepsilon_{\perp} = (a_{\perp} - a_{bulk})/a_{bulk}$ for out–of plane strain. The values of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ (Table 1) confirmed that LSMO films on LAO are compressed biaxially in in-plane and expanded in out-of-plane, LSMO films on STO are expanded biaxially in the film plane and compressed in out-of-plane. The LSMO films grown on LSAT exhibit only small strains and LSMO layers on MgO substrates are nearly fully relaxed because the in-plane lattice parameter is only weakly strained (0.2%) and the out-of-plane lattice parameter is equal to the bulk value of the LSMO.

The correlation of $\varepsilon_{\perp}$ vs. $\varepsilon_{||}$ in the LSMO films grown on different substrates is shown in Fig. 3 where a linear dependence is apparent. A similar behavior was presented in Ref. [1]. The linear dependence $\varepsilon_{\perp}$ vs. $\varepsilon_{||}$ indicates a strong influence of the substrate induced strain without interfacial effects. The strains $\varepsilon_{\perp}$ and $\varepsilon_{||}$ are coupled through Poisson's ratio $\nu = 1/(1\text{-}2\varepsilon_{||}/\varepsilon_{\perp})$, where $\varepsilon_{||}/\varepsilon_{\perp}$ can be determined from the $\varepsilon_{\perp}$ vs. $\varepsilon_{||}$ dependence. The estimated Poisson's ratio $\nu \approx 0.39$ corresponds with other presented data of $\nu = 0.37$ and $\nu = 0.35$ [1,6].

The quantification of strain dependence of magnetic (electrical) properties was performed folowing Millis et al. [12]. They consider two strain parameters: bulk compression ε_B and biaxial distortion ε_{JT} which influence the T_C. In the case of cubic symmetry, these parameters can be written as $\varepsilon_B = {}^1/_3\,(2\varepsilon_{||}+\varepsilon_{\perp})$ and $\varepsilon_{JT} = ½\,(\varepsilon_{\perp} - \varepsilon_{||})$. The predicted relation of the dependence T_C on strain is $T_C(\varepsilon_B,\varepsilon_{JT}) = T_C(0,0)\,(1 - \alpha\varepsilon_B - ½\Delta\varepsilon_{JT}^2)$, where $\alpha = 1/T_C(0,0)\,dT_C/d\varepsilon_B$ and $\Delta = 1/T_C(0,0)\,d^2T_C/d(\varepsilon_{JT})^2$. The second term (bulk strain) of the equation can be either positive or negative depending on the sign of $\varepsilon_{\perp}$ and $\varepsilon_{||}$ (Table 1), so this term can either contribute negatively or positively to T_C. The third term (Jahn-Teller term) always reduces the T_C (for $\varepsilon_{JT} \neq 0$); due to the sensitivity of material properties to strain a 10% reduction of T_C occurs at approximately 1% biaxial strain [12]. Usually, the competition between these two terms results in a moderate reduction of T_C. Our observed T_C values are plotted with respect to ε_B and ε_{JT}^2 in Fig. 4 and fitted using the equation for $T_C(\varepsilon_B,\varepsilon_{JT})$. The parameters obtained from the fit are: $T_C(0,0) = 431.91$ K, $\alpha = 39.97$, and $\Delta = 158.12$.

In the case of $La_{0.67}Sr_{0.33}MnO_3$ films, there is a considerable disagreement in the literature on the values of α and Δ. α ranges from 0.66 [8] to 10 [2], typically $\alpha = 6$ [12]. The parameter Δ ranges from 70 [3] to 2100 [6], typically 1400 [1,2,12], however, the authors [12] consider the value of 1400 anomalously large. The values of parameter $T_C(0,0)$ or $T_{MI}(0,0)$ were presented from temperature interval 330–370 K [1–3,6,8]. Since the third term of the equation always reduces the T_C (T_{MI}), only the second term can explain the increased values of T_C (T_{MI}). We estimated the possible increase of T_C (T_{MI}) to 392 K from the typical values of α (~6), ε_B (~1%) and $T_C(0,0)$ (~370 K). This is significantly lower than our experimentally observed T_C (T_{MI}). Moreover, the parameter $T_C(0,0) = 431.91$ K is