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Stress and defect induced enhanced low field magnetoresistance and dielectric constant in $La_{0.7}Sr_{0.3}MnO_3$ thin films

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ABSTRACT

Colossal magnetoresistive manganite $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) films were prepared by pulsed laser deposition on three different single crystal substrates using different deposition parameters. Characterizations of their surface morphologies, structural, magnetic and magneto-transport properties show that films on MgO single crystal substrates contain higher amount of structural defects compared to those on $SrTiO_3$ (STO) and $NdGaO_3$ (NGO) substrates. Low deposition rate and thicker films give rise to polycrystallinity and grain boundaries. The films on MgO substrate showed a broad paramagnetic (PM) to ferromagnetic (FM) transition accompanied with metal–insulator transition (MIT) much below their Curie temperature (T_C) indicating growth of strained structures due to large lattice mismatch (9%) between the substrate and the film. The deposited films on STO and NGO show least effect of substrate induced strain exhibiting sharper PM–FM transition and metallic behavior below T_C. The magnetoresistance (MR) measured with 300 mT field clearly shows two contributions, one due to grain boundary tunneling and the other due to colossal MR effect. The highest low field MR effect of 17% was achieved for the film on MgO with the highest thickness and surface roughness indicating the presence of grain boundary related defects. Also a high dielectric constant was observed for the same film at room temperature up to 100 kHz frequency. Coexistence of defect induced large low-field MR and abnormally high dielectric constant can give rise to different exciting applications.

1. Introduction

Colossal magnetoresistance (CMR) in perovskite manganites has been a subject of intense research interest since late 1990s [1,2]. The family of manganites are not only interesting because of their potential applications in magnetic field sensing and memory devices but also their fascinating and intriguing physics [3,4], not completely explored so far and exciting new results are emerging constantly [5,6]. The hole-doped manganites of general composition $Re_{1-x}A_xMnO_3$ (Re = rare-earth metal, A = divalent alkali metal) shows the coexistence of different phases and depending on the composition and structural defects, these phases can be modified significantly. The transition from insulator–metal phase is generally associated with paramagnetic (PM) to ferromagnetic (FM) phase change. The FM ordering in the hole doped materials are due to mixed valence state of Mn ions, mainly in form of Mn^{3+}–O–Mn^{4+} and the interaction between them by Zener double exchange mechanism. Among different hole-doped manganites, the half-metallic manganite $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) is possibly the most widely studied material as it has completely spin polarized conduction band at Fermi energy at low temperature, giving rise to 100% spin polarization. This half-metallic character has been successfully used for the spin injecting electrode in inorganic/organic spintronic devices [7,8]. Where as spintronic application requires, high quality epitaxial thin film sample with extremely smooth surface for a defect free interface between FM/non-magnetic junctions, structural defects, strains and surface roughness could also lead to interesting effects.

Due to mismatch between the film and substrate lattice parameters and oxygen non-stoichiometry in the lattice arising from improper growth conditions, the unit cell lattice is often stressed and these strained lattice structures give rise to deformed MnO_6 octahedra and thus the FM interaction and electronic conductivity is suppressed. Also the substrate induced stress causes misorientation of crystal lattice causing grain-boundary (GB) related defects. Different film growth parameters also play an important role on structural defects. One of the main defect-induced effect in polycrystalline thin-film and bulk manganite samples is the low-field magnetoresistance (LFMR) effect [9,10]. LFMR is very important for the magnetic field sensing application. LFMR has mainly been explained by the tunneling of spin polarized electrons between

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Table 1
Sample names, their characteristic deposition parameters and approximate thicknesses.

Sample	Temperature (°C)	No. of pulses	Frequency (Hz)	Approximate thickness (nm)
S1	780	10 000	5	400
S2	780	5 000	5	200
S3	780	10 000	10	400
S4	780	15 000	10	500
S5	700	5 000	10	200

FM grains separated by GB regions. To clarify the role of these GBs, arising either from the substrate induced strain or misoriented grains due to lack of proper growth conditions, on the magnetic and electronic properties of LSMO, we have fabricated LSMO films on different substrates starting from highly lattice-mismatched MgO (∼9%) to most closely matched $SrTiO_3$ (STO) (0.87%) and $NdGaO_3$ (NGO) (−0.2%) using different pulsed laser deposition (PLD) parameters and characterized their surface morphology, structure, magnetic and transport properties thoroughly. Varying the substrates and deposition parameters, both epitaxial and less-textured films are prepared for three different thicknesses on each substrate and comparison between their different properties give the opportunity to investigate how the defect induced magnetic and transport properties evolve from highly epitaxial films to less-textured films.

2. Experimental

Preparation of stoichiometric LSMO target material for pulsed laser deposition (PLD) was reported earlier [11]. Phase purities of the PLD targets were checked by X-ray diffraction (XRD) using Cu Kα radiation. LSMO films were grown on the MgO (1 0 0), STO (1 0 0) and NGO (1 0 0) polished single crystal substrates at temperatures (T_S) of 700 °C and 780 °C using the laser repetition rates of 5 Hz and 10 Hz and the pulse energy of 2 J/cm^2. The target to substrate distance was 35 mm and oxygen pressure in the deposition chamber was 0.25 Torr. These two parameters were chosen by observing the optimum plume formation and were kept constant for all the films. Films with different thicknesses were obtained by using 5 000, 10 000 and 15 000 pulses and the approximate thicknesses are 200, 400 and 500 nm, respectively. On each substrate, five LSMO films, deposited by different deposition parameters, were grown, as listed in Table 1.

After deposition, the films were subjected to post-annealing treatments in 1 atm pressure of oxygen for 10 min at the deposition temperature and then cooled to room temperature at the cooling rate of 20 °C/min. The surface morphologies of the films were characterized by atomic force microscopy (AFM) in non-contact mode and their compositions and lattice structures were investigated by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Model Philips PW3710). The magnetic properties were investigated with a SQUID magnetometer in the range of 5–400 K. The resistivities were measured using the four probe method in the range 5–300 K in the absence and presence of a magnetic field of B = 300 mT and LFMR were measured by sweeping the in-plane magnetic field between −300 and +300 mT and back at a fixed temperature. The impedance spectra were measured at room temperature with a Gamry 600^{TM} Potentiostat in a frequency range of 1 Hz to 1 MHz. The amplitude of the AC bias was 20 mV rms. The DC bias was varied from 0 to 1 V.

3. Results and discussion

3.1. Surface morphology

Fig. 1 shows the surface structures of the LSMO films deposited on different substrates. Although the surface features of the films were initially identified as almost similar [11], more detail inspection reveals that films grown on MgO have bigger domains compared to the surface structures of the films grown on STO and NGO. Also, the domains are more closely packed in the films on STO and NGO compared to that on MgO, where the domains have more island type growth. These features remain unchanged when the films were prepared by varying the frequency of the PLD pulses and T_S. However, the rms roughnesses of the films differ significantly due to variation in both the PLD pulse frequency and T_S.

Surface rms roughness values for as-grown films are calculated as an average from AFM images taken from different 5 μm × 5 μm areas of the films and the standard deviation in rms roughness value is ±1.2 nm, 1.0 nm and 0.4 nm for MgO, STO and NGO, respectively. The roughness increases with thickness in all substrates. Lower deposition temperature leads to the smoothest surface for all the substrates, especially on STO. For films on MgO, STO and NGO, the rms roughness is 9 nm, 3.7 nm and 9.1 nm, respectively, for T_S = 700 °C. However, the roughness value increases appreciably reaching 18.6 nm, 15 nm and 14.4 nm, respectively, for T_S = 780 °C. In addition, the higher deposition frequency (10 Hz) also leads to the smoother surface especially for films on STO and NGO. This leads to the conclusions that lower laser frequency, higher deposition temperature and increasing film thickness lead to more structural defects in the films. This could be explained with the difference in growth mechanisms affected by the different deposition parameters as well as the lattice mismatch between the film and the substrate [12,13].

3.2. Structural analysis

The room temperature XRD measurements show that the crystalline structure of the LSMO target is rhombohedral perovskite with space group $R\bar{3}C$ and lattice parameters a_h = 0.5473 nm and

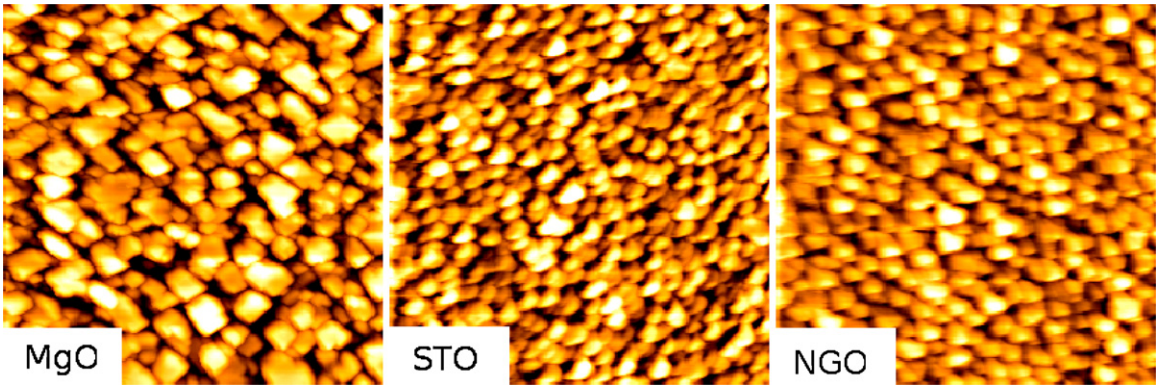

Fig. 1. AFM images (5 μm × 5 μm) of the LSMO films deposited on MgO, STO and NGO substrates with T_S = 780 °C, 10 000 laser pulses with frequency of 10 Hz. The grey scale (height from black to white) is 70 nm for all the films on MgO, STO and NGO.