Physica B: Condensed Matter 534 (2018) 141–144

Contents lists available at ScienceDirect

Physica B: Condensed Matter

journal homepage: www.elsevier.com/locate/physb

Magnetoelectric coupling in oxygen deficient $La_{0.67}Sr_{0.33}MnO_{3-\delta}/BaTiO_3$ composite film

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ARTICLE INFO

Keywords:
Ferroelectrics
Thin films
Multilayer structure

ABSTRACT

The effect of magnetic field on the polarization and dielectric properties in oxygen deficient $La_{0.67}Sr_{0.33}MnO_{3-\delta}/BaTiO_3$ composite film are investigated. A temperature dependent polarization variation induced by the magnetic field is observed. Under a magnetic fields of 0.8 T, the enhancement of saturation polarization is remarkable at low temperature region with a maximum changing rate 66.5% occurring at 70 K, whereas it is indistinctive at high temperature. The composite film also exhibits significant magnetodielectric property. The positive changing rate of dielectric constant η_ε induced by 0.8 T magnetic field reaches the maximum of 80% and 57% at 80 K with the frequency of 1 kHz and 100 kHz, respectively, and the corresponding changing rate of dielectric loss get the negative peak of −27% and −22%. The magneto-induced polarization and dielectric change may result from the charge-based coupling as well as the Maxwell-Wagner effect in this heterojunction.

1. Introduction

Magnetoelectric composite film is an important type of multiferroic materials, which is usually composed of typical ferromagnetic and ferroelectric materials [1–6]. For the ferroelectric layer, $BaTiO_3$ (BTO) attracts much attention for the lead-free characteristic. For the ferromagnetic layer, doped manganite ($R_{1-x}A_xMnO_3$) have been a good candidate to design advanced multiferroic films [7,8]. Multiple interactions among the freedom degrees of charge, orbital, spin and lattice inside the doped manganite [9,10] bring much additional properties into the manganite based composite films. It has been reported that the magnetoresistance of the manganite layer is remarkably enhanced by the effect of ferroelectric layer in $Pr_{0.85}Ca_{0.15}MnO_3/Ba_{1-x}Sr_xTiO_3$ system [11]. A magnetocapacitance is observed in $La_{0.7}Ca_{0.3}MnO_3$/-$Ba_{1-x}Sr_xTiO_3$, and the maximum value occurs at the phase transition temperature of the ferroelectric layer [12]. In $La_{0.7}Ca_{0.3}MnO_3/BaTiO_3$ and $La_{0.7}Sr_{0.3}MnO_3$/BTO, the magnetic phase transition temperature is raised by the biaxial tensile in-plane strain [13]. Wang et al. [14] reports that the voltage tunability in low frequency has a dominating contribution from the interfacial polarization. Li et al. [15,16] found that the magnetoelectric voltage coefficient of $La_{0.7}Sr_{0.3}MnO$/BTO composite film grown on $SrTiO_3$ can goes up to 263 mV cm^{-1} Oe^{-1}. At present, most research on manganite/BTO focus on the stoichiometric oxygen ion in manganite (Mn:O ~ 3:1), in which the manganite film is deposited on relative high oxygen pressure to avoid oxygen deficiency and the metal-insulator transition temperature (T_{MI}) near around the value in the electric/magnetic phase diagram [17,18]. While, the oxygen deficiency can not only adjust the properties of manganite itself, but also its heterojunction, such as the enhancement of photoconductivity in the $La_{0.6}Ca_{0.4}MnO$/Si heterojunction [19]. Therefore, abnormal magnetoelectric properties are expected in a oxygen deficient manganite/BTO composite film.

In this work, oxygen deficient $La_{0.67}Sr_{0.33}MnO_{3-\delta}/BaTiO_3$ (LSMO/BTO) composite film is prepared, and the magneto-induced polarization changing and magnetodielectric properties are investigated.

2. Experimental

The LSMO/BTO film was prepared on $SrTiO_3$ 100 substrates by Pulse laser deposition (PLD) method, and the designed structure is schematically presented in the inset of Fig. 1(a). The wavelength of the laser used in the film preparation is 248 nm. During the deposition, the pulse energy of 140 mJ and the frequency of 3 Hz was applied. The bottom LSMO layer was firstly deposited at 1073 K with an oxygen pressure of 5 Pa, The BTO film was grown at 1023 K at an oxygen pressure of 20 Pa. The thickness of LSMO and BTO layers was measured to be 100 and 120 nm respectively by a SpecEI-2000-VIS ellipsometer. The crystal structure was determined by Panalytical X'Pert X-Ray diffractometer (XRD). Topography of the

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https://doi.org/10.1016/j.physb.2018.01.051
Received 25 September 2017; Received in revised form 11 December 2017; Accepted 22 January 2018
Available online 3 February 2018

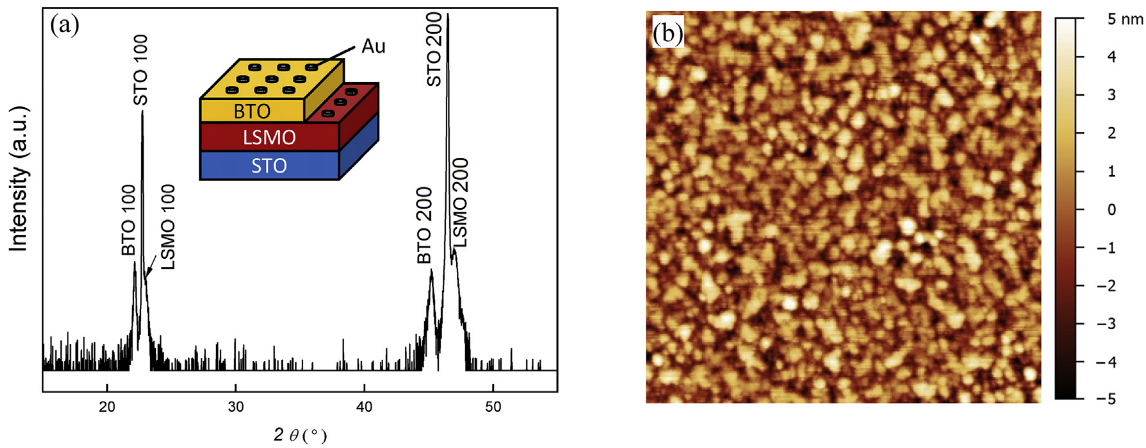

Fig. 1. (a) XRD pattern of LSMO/BTO bilayer film. The inset shows the schematic of sample structure. (b) Topography of BTO film in $2 \times 2\,\mu m^2$.

upper BTO layer was scanned with the Asylum MFP-3d atomic force microscope (AFM). The magnetization is measured by Quantum Design superconducting quantum interference device (SQUID). Au electrodes with diameter of 200 μm were deposited on the top surface, and the resistance of bottom LSMO was measured by Keithley 2400 m. Ferroelectric hysteresis loop was measured by Radiant Precision-LC ferroelectric test system. Dielectric properties is measurement by KEYSIGHT E4980A LCR meter. The temperature of the sample was controlled by a Janis CCS-300 closed-cycle refrigerator cryostat system in the temperature range from 30 to 300 K. The external magnetic field can be adjusted in a intensity range of 0–0.8 T.

3. Results and discussion

XRD pattern of the composite film is shown in Fig. 1(a). Both of LSMO and BTO peaks appear near around the substrate STO peak, revealing good epitaxial growth of this bilayer film. The LSMO peaks exist at 23.0° and 46.9°, which are nearly the same diffraction angles as those of the rhombohedral $La_{0.67}Sr_{0.33}MnO_3$ (0 1 2) and (0 2 4) in the standard PDF card. This indicates a very weak in-plane strain of the LSMO film from STO substrate. Meanwhile, two BTO peaks locate at 22.1° and 45.2°, which correspond to (1 0 0) and (2 0 0) faces in tetragonal structure. Fig. 1(b) show the topography of upper BTO layer, whose root mean roughness is determined to be 1.1 nm.

It is known that the metal-insulator transition of normal $La_{0.67}Sr_{0.33}MnO_3$ occurs at ~350 K, and this transition temperature can be reduced or even disappear with oxygen deficiency increases [20]. Here, the upper LSMO film exhibits semiconductive characteristic ($dR/dT < 0$) in the temperature range of 30–400 K (Fig. 2(a)), indicating that the heterojunction is fabricated with oxygen deficient LSMO film and BTO as expected. When applied a magnetic fields of 0.8 T, a decreasing of the resistance in LSMO is observed. The changing rate $MR=(R_{0.8T} - R_{0T})/R_{0T}$ decrease from 45.28% at 30 K to 0.15% at 400 K, as shown in Fig. 2(a). The magnetization of LSMO is shown in Fig. 2(b) in which LSMO exhibit ferromagnetic at 300 K (the inset of Fig. 2(b)), and no magnetic phase transition occurs in the temperature range from 20 to 300 K. It proves that the magnetic transition occurs above 300 K, and LSMO keeps ferromagnetic state in the range of 20–300 K.

The polarization-electric field (*P-E*) hysteresis loop of BTO was measured with 0 T and 0.8 T magnetic field in the temperature range from 30 to 300 K, and the typical *P-E* loop is show in Fig. 3(a) and (b). It can be observed that not only the shape of *P-E* loop is changed with the various temperatures, but also the effect of magnetic field on the ferroelectric polarization. At 90 K, the saturation polarization (*Ps*) are remarkable enhanced by the magnetic field, while, the coercive electric field (E_c) is depressed. At 210 K, the change of *P-E* loop induced by the magnetic field is very weak. Fig. 3(c) shows the statistics of *Ps* versus temperature. *Ps* monotonously decreases with the decreasing temperature from 300 to 30 K both under 0 T and 0.8 T magnetic field. With the decreasing temperature, the changing rate of the saturation polarization, $\eta_P = (Ps_{\ 0.8T} - Ps_{\ 0T})/Ps_{\ 0T} \times 100\%$ increases from ~1% at 300 K to the maximum value of 66.5% at 70 K, then sharply decreases to 18.6% at 30 K. The coercive electric field (*Ec*) firstly increases to the maximum value at 50 K, then decreases. The maximum of the changing rate $\eta_E = (Ec_{0.8T} - Ec_{0T})/Ec_{0T} \times 100\%$ occur at 110 K.

Based on the phenomenon above, we can indicate that abnormal

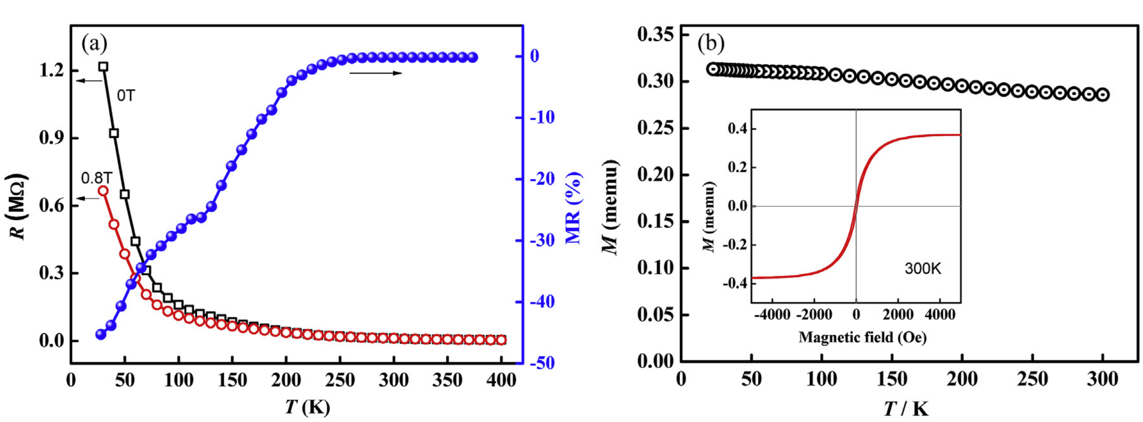

Fig. 2. Transportation and magnetic properties of LSMO film: (a) In-plane resistance of LSMO layer with and without magnetic field; (b) variable temperature magnetization of LSMO film, and the inset is the hysteresis at 300 K.