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Polarization-induced electro resistance and magneto resistance in $La_{0.67}Ca_{0.33}MnO_3/BaTiO_3$ composite film

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ABSTRACT

$La_{0.67}Ca_{0.33}MnO_3/BaTiO_3$ composite films have been grown on Nb-doped $SrTiO_3$ substrates by the sol–gel method. The magnetic and ferroelectric properties in the composite films are investigated. A three-state memory is formed by applying a vertical electric field across the $La_{0.67}Ca_{0.33}MnO_3/BaTiO_3$ heterostructure, this behavior is attributed to the polarization-mediated resistive switching effect. In addition, the transport properties of $La_{0.67}Ca_{0.33}MnO_3$ thin film can be modulated by an external magnetic field, a 10.3 K shift of the metal insulator transition temperature is obtained with the change of applied magnetic field from 0 T to 6 T. Consequently, in $La_{0.67}Ca_{0.33}MnO_3/BaTiO_3$ heterostructure, the resistance behavior can be modulated by piezoelectric effect, ferroelectric polarization and magnetic field simultaneously.

1. Introduction

Ultrafast operating speeds, low power consumption and simple structure will be the key features for the next generation of highly integrated memory devices used in high-performance computing. As contemporary memory technologies such as flash memory are approaching their technological and physical miniaturization limits, it will be difficult to continue to improve the performance. Emerging resistive switching memory devices based on the displacement or diffusion of ions have attracted more great interest, owing to its advantages of high-density integration, fast switching, low energy consumption, and etc [1–3]. At first, the resistive switching phenomena have been observed in capacitor-like metal/insulator/metal (MIM) structures consisting of various transition metal oxides [4], and some possible mechanisms have been proposed such as conductive filament model [5]. Then, some studies found that carbon-based materials [6], ferrites [7] can also be used as the active layer ("I") in the MIM structure. In recent years, the resistive switching behavior of multiferroic materials have drawn more and more researchers' attentions [8], because it offers additional degrees of freedom for multiferroic-based multifunctional devices. As previously reported [9,10], multiferroic-based materials have a series of excellent performance. However, the few known natural multiferroics present weak coupling between the electronic and magnetic degrees of freedom. By contrast, artificial multiferroic heterostructures can combine optimal ferromagnetic and ferroelectric properties. Stronger coupling effect make artificial composite multiferroic materials more conducive to practical applications. The doped manganites are strongly correlated electron system with charge, orbital, and lattice degrees of freedom. $La_{0.67}Ca_{0.33}MnO_3$ (LCMO), as a typical representative of them, have phase transition from ferromagnetic metal to paramagnetic semiconductor around 250 K. At the same time, since the location of manganites on the phase boundary, it is sensitive to the external field including magnetic field, electrical field, current, and light. $BaTiO_3$ (BTO), as a typical environmentally-friendly ferroelectric material, display a mixture of tetragonal and cubic phases, the so-called strain effect can be used for regulating other films' properties [11,12]. Therefore, LCMO/BTO composite thin film is chosen as the study subject. The devices combining ferroelectric BTO and ferromagnetic LCMO manganites are prone to phase separation, and their interface with ferroelectrics has been shown to exhibit a rich phenomenology, both experimentally and theoretically [13,14].

Recently, in addition to the study on resistive random access memory (RRAM) of traditional MIM structures, switching of various physical parameters (resistance, electrical conductivity, magnetization, luminescence, etc.) between different states by controlling the strain or

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ferroelectric polarization have become a growing concern, these experiments point to a pathway for creating some functionalities. Among them, the resistive switching behaviors of the films grown on PMN-PT substrates have received great attentions, due to the lattice parameters of PMN-PT can be changed regularly by applying electric fields because of the converse piezoelectric effects, which is intriguing for the potential application in memory devices. The non-volatile reversible resistive switching behaviors have been observed in corresponding heterostructures, such as Fe_3O_4/PMN-PT [15], VO_2/PMN-PT [16,17] and LCMO/PMN-PT [18]. In this study, in addition to be induced by piezoelectric effect, we demonstrate the resistive switching behaviors can also be controlled by ferroelectric polarization. Different resistance states of LCMO layer are detected by changing the polarization direction of BTO layer. In addition, the modulation effect of the external magnetic field on the transport properties of LCMO thin film have also been observed. A 10.3 K shift of the metal insulator transition temperature is obtained with the change of applied magnetic field from 0 T to 6 T.

2. Experimental details

BTO thin films with a thickness of 500 nm were fabricated on Nb-doped $SrTiO_3$ (NSTO) substrates by the sol–gel method. Firstly, 0.006 mol $(CH_3COO)_2Ba$ were added in 6 mL acetic acid, under stirring at 60 °C to form a homogeneous solution 1; Secondly, 0.006 mol Tetra-n-butyl Titanate ($C_{16}H_{36}O_4Ti$) were added in 3 mL acetylacetone ($C_5H_8O_2$), continue stirring until fully dissolved to obtain solution 2; Then, the solution 1 was dropped into ethylene glycol monomethylether ($C_3H_8O_2$), after stirring for several minutes, the solution 2 was dropwise added, the precursor solution was prepared after fully mixing for 30 min. After placing at room temperature and aging for several hours, the films were prepared by spin-coating the deposition solution onto an Nb-doped $SrTiO_3$ substrate. The precursor solution was spin-coated at 3000 rpm for 30 s and pre-sintered at 380 °C for 5–10 min in air. This process was repeated several times to obtain a desired film thickness, and at last the film was annealed at 1000 °C for 1 h in air atmosphere. Subsequently, LCMO thin films with a thickness of 180 nm were fabricated upon BTO thin film by the sol–gel method. The precursor solution of LCMO was prepared by dissolving an 0.8:0.2:1 mol ratio mixture of $La(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$ and $Mn(NO_3)_2$ in ethylene glycol monomethylether ($C_3H_8O_2$); then, a small amount of acetic acid as chelating agent were added to eventually obtain 20 mL solution. After aging for several hours, the films were prepared by spin-coating from the deposition solution onto BTO thin film. At last, the samples were annealed at 1000 °C for 1 h in air atmosphere. All the chemicals were of analytical grade purity and were used as received without further purification.

To measure the electrical properties of the composite films, Pt top electrodes, 0.1 mm in diameter, were deposited with a shadow mask via magnetron sputtering method. The as-synthesized samples were characterized by an X-ray diffractometer (XRD, X′ Pert PRO PHILIPS with Cu K_α radiation, $\lambda = 1.54056$ Å). The morphologies of the samples were characterized using scanning electron microscopy (SEM, Hitachi S4800). The magnetism at different temperature was studied via a superconducting quantum interference device (SQUID, MPMS XL, Quantum Design Company, San Diego, CA). The ferroelectric hysteresis loops were measured at 1 kHz at room temperature using a precision materials measuring system (Premier II; Radiant Technologies Inc., America). A Keithley 2400 and 6517B source measurement unit were employed to test the electrical properties of LCMO/BTO composite films. The pulse width was approximately 300 ms in our measurement. All tests were performed at room temperature.

3. Results and discussion

The XRD patterns of LCMO/BTO composite film are exhibited in

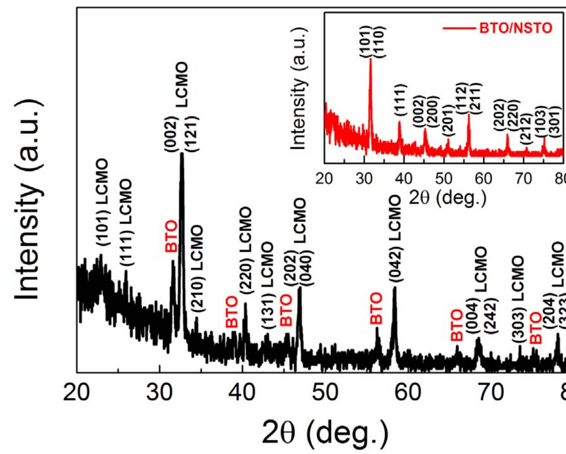

Fig. 1. XRD patterns of LCMO/BTO composite film.

Fig. 1, and the inset of Fig. 1 shows the XRD pattern of monolayer BTO thin film. Pure LCMO (JCPDS No. 49–0416) and BTO (JCPDS No. 05–0626) are detected, polycrystalline structures are obtained, and no other impurities peaks are found. Fig. 2(a) displays the surface SEM image of LCMO thin film, LCMO thin film is consists of nanoparticles, relatively uniform and flat surface is observed. The average grain size of LCMO thin film is around 80 nm. Compared with the LCMO thin film grown on NSTO substrate directly, the grain size is increased and the particle distribution is more uniform by inserting BTO layer. Fig. 2(b) shows the cross-sectional SEM images of LCMO/BTO/NSTO heterostructure, the compact degree of cross section is fairly high. Both LCMO and BTO thin films are well grown on NSTO substrate, with thicknesses of approximately 180 nm and 500 nm, respectively.

As depicted in Fig. 3(a), the magnetization versus magnetic field (*M–H*) curves are measured at 10 K and 300 K using a SQUID magnetometer, where the paramagnetic signal is subtracted. The saturation magnetization (M_S) increased with the decrease of temperature. This is because the thermal fluctuations can randomly change the orientation of the magnetic moment, with the decrease of temperature, the random thermal motion is reduced. Therefore, the degree of magnetic moment orientation is enhanced. Loops exhibit clear hysteresis from the insets in Fig. 3(a), in which the coercive field are $H_{C300} = 83.5$ Oe, $H_{C10} = 264.8$ Oe, respectively. Fig. 3(b) displays the ferroelectric loops for LCMO/BTO heterostructure measured at 0.1 kHz. A linear hysteretic behavior is measured for this sample, the remanent polarization (P_r) and coercive electric field (E_C) of LCMO/BTO heterostructure are 0.012 $\mu C/cm^2$ and 229.2 kV/cm, respectively. The values of P_r is fairly low and the *P–E* hysteresis loop is not saturated under a large enough electric field, indicating the absence of long-range ferroelectric ordering [19]. The poor ferroelectricity may be due to the poorer quality of the BTO thin film prepared by sol-gel method. Presumably, the high temperature rapid thermal annealing changed the microstructure (or the number of defects/oxide traps) [20], leading to the increase of the leakage current, which affect the ferroelectric properties of BTO thin film.

To investigate the low-temperature ferromagnetic properties of the composite films, the temperature dependences of the dc magnetizations in ZFC (zero-field-cooled) and FC (field-cooled) modes from 1.9 to 300 K in a field of 100 Oe is performed in Fig. 4. The bifurcation between ZFC and FC branches is present even up to 300 K, which imply that the magnetic ordering temperature (T_C) of the composite films is higher than 300 K, the result is proved by the *M-H* curve as shown in Fig. 3(a). The ZFC curves of the composite films show a peak around $T_f \sim 100$ K and an obvious separation from the FC curve below T_f, which correspond to the freezing temperature (or blocking temperature) of the spin-glass-like behavior. The ZFC and FC curves deviate from each other, means that an antiferromagnetic phase exists in the