Leakage current transport mechanisms of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ bilayer films grown on Nb:SrTiO_3

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Abstract. $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ (LSMO/BTO) bilayer films were epitaxially grown on Nb:SrTiO_3 (NSTO) substrates by the pulsed laser deposition technique. Current–voltage (I – V) characteristics of the LSMO/BTO bilayer films were studied. I – V curves were measured at room temperature, which show rectifying behaviour and can be well fitted by the space-charge-limited current mechanism under forward bias while thermionic emission model under reverse bias. Analysis indicates that a modulating Schottky barrier exists at the LSMO/BTO interface, which dominates the leakage current transport properties of LSMO/BTO bilayer films.

Keywords. $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ films; leakage current transport mechanism; Schottky barrier.

1. Introduction

BaTiO_3 (BTO) is a typical ferroelectric material, which has wide applications in electronic, electro-optical and electromechanical devices. In recent times BTO films have been a focus of intensive studies in magnetoelectric coupling effect,¹ ferroelectric tunnel junctions (FTJs)² and artificial multiferroic tunnel junctions (MFTJs).^{3,4} BTO ultrathin films are usually active ferroelectric tunnel barriers sandwiched between metal electrodes or magnetic electrodes in FTJs and MFTJs, e.g., Pt, Co, Fe or $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO). Doped perovskite manganite LSMO films are considered to be excellent conductive layers, magnetic films at room temperature and well-fitted lattice parameters with BTO films and Nb-doped SrTiO_3 (NSTO) substrates.^{5–7} Moreover, compared with easily oxidized metal electrodes,^{3,8} LSMO films are more feasibly prepared by the pulsed laser deposition (PLD) method on oxide films or substrates, e.g., BTO and NSTO.

Scanning probe microscopy techniques are used to quantify the current transport properties of FTJs and MFTJs such as scanning tunneling microscopy (STM) and conducting atomic force microscopy (C-AFM).^{4,6,9} Although there are studies reported on the interface structures of BTO/LSMO,^{6,9} the relationship between the properties of current transport and interface barrier of BTO/LSMO is seldom investigated. Furthermore, oxygen deficiency such as oxygen vacancies is inevitable more or less in BTO films which are grown under lower oxygen pressure.¹⁰ Oxygen vacancies in such

BTO films have a distinct role to the current transport of metal/BTO in the resistive switching random access memories (RRAMs),¹¹ which should also be considered in above-mentioned junction devices with LSMO ferromagnetic electrodes.

In this paper, LSMO/BTO bilayer films were deposited on 0.7 wt% Nb-doped SrTiO_3 single-crystal substrates by PLD. The leakage current transport properties were investigated considering the modulating Schottky barrier at the interface of LSMO/BTO as demonstrated by I – V curve fittings, which will give detailed information on the electronic structure of interface and the properties of leakage current transport in such ferromagnetic/ferroelectric hybrid devices.

2. Experimental

LSMO and BTO thin films were successively prepared on NSTO (001) single-crystal substrates at 700°C by PLD. The electrical resistivity of NSTO substrates is about 7.0 mΩ cm at room temperature. The NSTO substrates were chemically cleaned and annealed at 1100°C for 10 h in air before the deposition in order to get atomically smooth surface.¹² A KrF excimer laser (the wavelength is 248 nm) operating at 2 J cm^{–2} was focused on the surfaces of a rotating LSMO powder target (which was obtained by the pressing method after pure LSMO powder was calcined at 900°C) and BTO ceramic target at a 45° angle of incidence. NSTO substrates were placed on a heater, which was 50 mm away from the targets. The working pressure of O₂ flow for BTO films and LSMO films during the deposition was maintained at 1.0 and 30 Pa, respectively. As-prepared LSMO/BTO samples were annealed in a tube furnace in air.

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The crystalline structure of LSMO/BTO films was analysed by an X-ray diffractometer (XRD: Rigaku, D/MAX-RB) with Cu K α radiation ($\lambda = 0.15405$ nm). Prepared LSMO films were measured by the four-wire resistance measurements method using a commercial physical property measurement system (PPMS: Quantum Design). The thicknesses of BTO and LSMO films were indirectly measured by comparing with the corresponding thicker films (above 500 nm, measured by a surface profiler, Taylor Honson, S4C-3D).

I - V characteristic measurements were performed by a ferroelectric parameter test system (Precision Premier II: RT) at room temperature. Before I - V measurement, 100-nm-thick Au layers patterned by a metal mask (diameter 0.5 mm) were deposited on the LSMO films and NSTO substrates at room temperature by magnetron sputtering. To test whether it is Ohmic contact of Au/LSMO or Au/NSTO, I - V measurements were also carried out by indium electrodes (about 0.5 mm²) pressed on the LSMO films and NSTO substrates, respectively. To avoid exceeding the limit current of the measurement system, the highest bias voltage was limited to 4 V.

3. Results and discussion

XRD patterns displayed in figure 1 show that only (00 l) diffraction peaks of the LSMO and BTO films are observed. No other peaks can be detected, which indicates that high-quality LSMO and BTO films are epitaxially grown on NSTO substrates. The thicknesses of LSMO and BTO films are both 100 nm.

Forward bias applied to the films is defined as the leakage current flowing from the top electrode Au into the LSMO/BTO films (see the right inset in figure 2). I - V curves in figure 2 show rectifying character, which implies that the

Figure 1. XRD pattern of the LSMO/BTO bilayer films grown on NSTO substrates.

electrode/film contacted with BTO film have different work functions or non-negligible interface barrier.¹³ The left inset in figure 2 shows that LSMO films are in the metallic state at room temperature. We tested the in-plane I - V curves of LSMO and BTO films with In (pressed) and Au (sputtering deposited) electrodes, respectively, as shown in figure 3. The absence of non-linearities in the I - V curves of figure 3 manifest that Schottky barrier height (SBH) can be neglected in the interface of Au/LSMO or Au/NSTO, which are due to the high carrier densities in LSMO and NSTO,^{13,14} the small difference in the work functions of Au and LSMO and/or sizeable charge injection effects.¹⁵ Au electrodes are Ohmic contacted with LSMO and NSTO films, respectively, according to figure 3. So in the following discussion, LSMO (NSTO) will be regarded as top (bottom) electrode.

I - V curves are re-plotted to probe leakage current transport properties of the LSMO/BTO/NSTO structure. Under forward bias (see figure 4a), the I - V curve exhibits three distinct regions where the slopes of $\ln I \sim \ln V$ curve are different. Firstly, as the forward bias is low (<0.4 V), the slope is unity implying that Ohmic conduction is the dominant mechanism. In this region, the total density of free-electrons is almost the thermal equilibrium electron density.^{16,17} Secondly, as the forward bias increases (0.4–0.8 V), the current sharply ascends. This region with high slope is called trap-field-limited (TFL) region.¹⁷ Thirdly, the slope drops from 7.8 to around 2.0. The third region is governed by the space-charge-limited current (SCLC),^{16–18} in which the current follows a square dependence on voltage: $I \propto V^2$ (Child's trap-free square law).¹⁷ Figure 4a shows that I - V curve on the logarithmic scale is bounded by three distinct lines which form the Lampert's triangle.¹⁷ The threshold voltages at the onsets of TFL region and trap-free space region have the

Figure 2. I - V curves in semi-log scale for the Au/LSMO/BTO/NSTO/Au structure. Maximum voltages are 1.0 V (open square), 2.0 V (open circle) and 4.0 V (open diamond), respectively. The left inset shows temperature-dependent resistance of the LSMO films. The right inset shows the measurement schematic of a conventional sandwiched structure (not to scale).

Figure 3. I - V curves of LSMO in-plane (open circle) and NSTO in-plane (open square), two-probe configuration was used.

relationship: $V_{T-Ch} = 2 V_{TFL}$, which has been confirmed in other reports.^{19–21}

Figure 4b shows that under low reverse bias ($0 \sim -1.0$ V), the slope of $\ln(-I) - \ln(-V)$ curve is also unity implying the Ohmic conduction mechanism. As reverse bias increases (< -1.0 V), the slope becomes bigger. The $\ln(-I) \sim (-V)$ curve in the inset of figure 4b shows a linear relationship, which exhibits a thermionic emission characteristic.¹⁶

Figure 5 shows schematic band diagrams of the LSMO/BTO/NSTO structure. The work functions for LSMO and NSTO are 4.8 and 4.1 eV, respectively.²² The band gaps of BTO and NSTO are almost same (about 3.2 eV) and the difference between the work functions 4.1 (NSTO) $-$ 3.9 (BTO) $\approx$ 0.2 eV is small.^{23,24} The barrier height at the interface of LSMO/BTO is about 0.9 eV, which is the dominant contribution to the rectifying behaviour of I - V curves in figure 2. As forward bias is added, SBH of the interface of LSMO/BTO decreases,^{16,25} which allows electrons to inject from NSTO into BTO easily and then be trapped in BTO films by oxygen vacancies and other defects. This is consistent with SCLC mechanism. Xia *et al.*²⁶ reported that Pt/Ba_{0.5}Sr_{0.5}TiO₃/LSMO/Pt structure also has similar leakage current transport properties, in which the leakage current of Ba_{0.5}Sr_{0.5}TiO₃/LSMO interface was governed by Ohmic conduction under low bias and SCLC mechanism under higher bias. Under reverse bias, SBH of the LSMO/BTO interface increases. However, the Schottky barrier near the BTO/NSTO interface decreases and can even collapse under high positive bias.²⁷ Thermionic emission can occur when the shape of the barrier profile is unimportant and the current flow depends solely on the barrier height.¹⁶

Figure 4. I - V curves of LSMO/BTO bilayer films in log-log scale under (a) forward bias and (b) reverse bias. The slopes of $\ln I \sim \ln V$ curves are added. The threshold voltages at the onsets of TFL region (V_{TFL}) and trap-free space region (V_{Ch-T}) are indicated.

Figure 5. Schematic band diagrams of the LSMO/BTO/NSTO structure under (a) zero bias, (b) forward bias voltage and (c) reverse bias.

At last, the leakage current may be larger in our prepared BTO films and no well-saturated hysteresis loops could be obtained. In this case the area of the interface may be too large and too leaky to accomplish switching even in the epitaxial films.^{10,28}

4. Conclusions

LSMO/BTO bilayer films are epitaxially grown on NSTO substrates by PLD. I - V characteristic of LSMO/BTO was described by SCLC and thermionic emission mechanisms under forward bias and reverse bias, respectively. The fittings of I - V curves indicate that modulating Schottky barrier exists at the interface of LSMO/BTO, which dominates the leakage current transport properties of LSMO/BTO bilayer films.

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