Acta Materialia 106 (2016) 40–47

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Structural, magnetic and magnetotransport properties of bi-epitaxial $La_{0.7}Sr_{0.3}MnO_3$ (110) thin films integrated on Si (001)

Sandhyarani Punugupati*, Raj Kumar, Sudhakar Nori, Frank Hunte, Jagdish Narayan

Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:
Received 13 November 2015
Accepted 31 December 2015
Available online xxx

Keywords:
$La_{0.7}Sr_{0.3}MnO_3$ (110)
Bi-epitaxial
Magnetoresistance
Out-of-plane

ABSTRACT

We report the growth of bi-epitaxial $La_{0.7}Sr_{0.3}MnO_3$ (110) thin films on Si (001) substrate with cubic yttria stabilized zirconia (c-YSZ)/$SrTiO_3$ (STO) buffer layers by pulsed laser deposition. The $La_{0.7}Sr_{0.3}MnO_3$ and STO thin films were grown with a single [110] out-of-plane orientation and with two in-plane domain variants, which is confirmed by XRD and detailed TEM studies. The growth of STO on c-YSZ can be explained by the paradigm of domain matching epitaxy. The epitaxial relationship between STO and c-YSZ can be written as [110] (001) c-YSZ ‖ $[\bar{1}1\bar{1}]$ (110) STO (or) [110] (001) c-YSZ ‖ $[\bar{1}1\bar{2}]$ (110) STO. The $La_{0.7}Sr_{0.3}MnO_3$ thin films are ferromagnetic with Curie temperature 324 K and showed metal to insulator transition at 285 K. The $La_{0.7}Sr_{0.3}MnO_3$ thin films showed hysteresis loops in magnetoresistance when magnetic field is applied along both in-plane (110) and out-of-plane [110] directions. The highest magnetoresistance obtained in this study is −32% at 50 K and 50 kOe for in-plane configuration, whereas the room-temperature magnetoresistance is −4% at 10 kOe and −17% at 50 kOe. The hysteresis in the magnetoresistance and the controlled domain boundaries in bi-epitaxial $La_{0.7}Sr_{0.3}MnO_3$ films integrated on Si can offer significant advantages over the polycrystalline counterparts.

1. Introduction

The doped manganese perovskites of the type $La_{1-x}Sr_xMnO_3$ have attracted great deal of attention due to their rich physics and fascinating magnetoresistance (MR) properties [1–3]. They are potential candidates to be used in the emerging technological applications such as magnetic read heads, magnetic resistance memory and other novel spintronic devices. In particular, the $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) is a hole doped half metal with a Curie temperature (T_C ~ 360 K) above room temperature. In LSMO and other manganites, huge MR, called colossal magnetoresistance (CMR) is observed close to T_C but at very high magnetic fields [4–6]. For device applications, the MR should be achieved at low fields and at or above room temperature. Following the observation of extrinsic low field magnetoresistance (LFMR) in polycrystalline bulk materials [7,8] and thin films [9–11], which possess natural grain boundaries, efforts are made to improve LFMR by introducing artificial grain boundaries. Nanocomposite films of LSMO with secondary phases such as ZnO [12–14], $BaTiO_3$ [15], and NiO [16] have been investigated for this purpose. We have introduced bi-epitaxial films (or) epitaxial films with domain boundaries in this study to achieve LFMR in a controlled way. Compared to the grain boundaries in polycrystalline and nanocomposite thin films, the domain boundaries in these films are well characterized having a fixed orientation relationship between the domains. Since boundaries play a significant role in controlling the transport properties, understanding their effect on transport properties can be useful to better design the devices for practical applications. The intrinsic CMR effect in manganite epitaxial films is explained by a theory which combines the John-Teller effect and double exchange mechanism [3,17,18]. In contrast, the extrinsic LFMR in polycrystalline and nano composite thin films is explained by spin-polarized tunneling [7,19] or spin-dependent scattering at the grain boundaries [10,20]. Though, Ramesh group has reported the effect of in-plane domains on the MR [21], the LSMO in their case was integrated on MgO substrate and also detailed magneto-transport properties study in such films is lacking. In addition, for the (110) oriented growth, there is no polar discontinuity at the STO–LSMO interface and hence no dead layer formation occurs. This improves ferromagnetic interaction in the LSMO, making it highly attractive for spintronic applications.

On the other hand, integration of perovskite STO thin films with

* Corresponding author.
E-mail address: spunugu@ncsu.edu (S. Punugupati).

http://dx.doi.org/10.1016/j.actamat.2015.12.054
1359-6454/

Si substrate is of technological importance for fabricating multifunctional devices on Si (100), the preferred substrate for microelectronics industry. By using molecular beam epitaxy, researchers succeeded in growing STO (100) directly on Si (100) [22–25]. PLD has been demonstrated to be effective for a controlled growth of STO (110) directly on Si (100) [26,27]. But in most of these cases, a thin intermediate layer of Sr-silicide/Sr-silicate forms which was crucial for the subsequent formation of the STO film [24–26]. The chemical and thermal stability of these layers and their influence on physical properties have to be considered for device applications. On the other hand, more stable and insulating buffer layers like ceria doped zirconia [28] and CeO_2/c-YSZ [29] were also used to grow epitaxial STO (110) films. In this study, the primary focus is on the details of bi-epitaxial growth and the role of domain boundaries on the magnetotransport properties. First we analyze the bi-epitaxial integration of LSMO (110) thin films on Si (001) using c-YSZ/STO buffer layers and study the atomic structure of the c-YSZ/STO interface. Second, we perform detailed study of the effect of domain boundaries in LSMO (110) thin films on the electrical, magnetic and magnetotransport properties.

We have integrated STO (110) bi-epitaxial films with Si (001) substrate using c-YSZ buffer. The growth of STO on c-YSZ takes place with two in-plane domain variants and can be explained by the paradigm of domain matching epitaxy (DME) [30], where integral multiples of lattice planes match across the film–substrate interface to accommodate the misfit under a large misfit conditions $\geq$10%. Here the critical thickness is less than a monolayer and misfit strain can be relaxed from the beginning so that the rest of the film can grow defect-free, except the thermal strain. The LSMO (110) films deposited on STO/c-YSZ/Si are ferromagnetic with T_C ~ 324 K and exhibit metal to insulator transition at 285 K. The easy axis of the magnetization lies in the LSMO (110) plane whereas the hard axis is along the out-of-plane [110] direction. The LSMO films showed hysteresis loops in MR measurements under applied field in both in-plane and out-of-plane directions. The temperature dependent MR showed a peak in low temperature region followed by a monotonic decrease up to 350 K. The highest MR obtained in this study is −32% at 50 K and 50 kOe for magnetic field parallel to the film plane whereas the room temperature MR is −4% at 10 kOe and −17% at 50 kOe. The hysteresis in MR and the controlled domain boundaries in bi-epitaxial $La_{0.7}Sr_{0.3}MnO_3$ films can offer significant advantages over the polycrystalline counterparts, where microstructure control presents a serious challenge in terms of reliability of solid state devices.

2. Experimental details

The LSMO/STO/c-YSZ/Si (001) heterostructure was grown in a multi target PLD chamber that utilized KrF laser of 248 nm wavelength and 25 ns pulse duration. The target to substrate distance was maintained at 4 cm during the deposition and the base pressure of the chamber before the deposition was less than 1×10^{-6} Torr. The laser energy density was 2.8 J/cm^2 for c-YSZ and 3.0 J/cm^2 for STO and LSMO whereas the repetition rate was 5 Hz for all the layers. The substrate was vapor cleaned in trichloroethylene at 200 °C and then ultrasonically cleaned by immersing in acetone and methanol each for 5 min. Initially after heating the substrate to 675 °C, the c-YSZ layer was deposited with 500 pulses under 1×10^{-5} Torr vacuum and the rest under 8.5×10^{-4} Torr O_2, and then oxygen partial pressure was adjusted to 1×10^{-2} Torr for the deposition of STO. After that the substrate was taken to 700 °C and LSMO was deposited at 3×10^{-1} Torr oxygen partial pressure. Once the deposition was completed, the sample was cooled down to room temperature at 10 °C/min under 5 Torr oxygen partial pressure. The phase structure of the films was determined by X-ray diffraction θ–2θ scans using Rigaku X-ray diffractometer with Cu K_α (0.154 nm) radiation. The JEOL 2010F TEM was used for imaging and to obtain selected area electron diffraction (SAED) patterns. The aberration corrected STEM–FEI Titan 80–300 was used for high-angle annular dark field (HAADF) imaging of the heterostructure. The cross-sectional TEM specimen was wedge polished until 1 μm thickness and then ion milled to electron transparency. The magnetic measurements were done using Quantum design Superconducting Quantum Interference Device (SQUID). Magnetotransport measurements were performed on 5 mm × 5 mm LSMO thin films in Quantum Design, EverCool-II PPMS. Four indium dots were mechanically pressed on the corners of the sample to perform four probe resistance measurements in van der Pauw configuration. The sample with pressed indium dots was mounted on a custom built rotatable pogo-pin setup in the PPMS. All the measurements were performed in AC delta mode with model 6000 PPMS controller to measure magnetoresistance accurately without any error in the measurements.

3. Results and discussion

The XRD 2θ scan acquired on the LSMO/STO/c-YSZ/Si heterostructure is shown in Fig. 1. The growth conditions for STO were optimized to achieve (110) plane on c-YSZ (001). At a substrate temperature of 670 °C, the STO thin film on c-YSZ (001) has a single [110] out of plane orientation. Since the LSMO (3.876 Å) is lattice matched with STO (3.905 Å), it resulted in the same orientation as STO. The STO (110) has a peak position at 32.364°, which corresponds to a lattice constant of 3.911 Å. Compared to the bulk lattice constant, the STO film is tensile strained about +0.1% along the out-of-plane direction, which is negligible. The details of the STO growth and strain analysis will be discussed later. The LSMO film is −1.7% compressively strained along the [110] out-of-plane direction as measured from the XRD 2θ-scan. All of the films exhibit a single out-of-plane orientation, inferring that as grown films are either highly textured or epitaxial in nature. In order to determine the crystalline and epitaxial characteristics, and the interface structure of the films, we have performed detailed cross-sectional transmission electron microscopy study of the heterostructure.

Fig. 2(a) shows the low magnification image of the heterostructure, where columnar grains of STO and the extension of grain

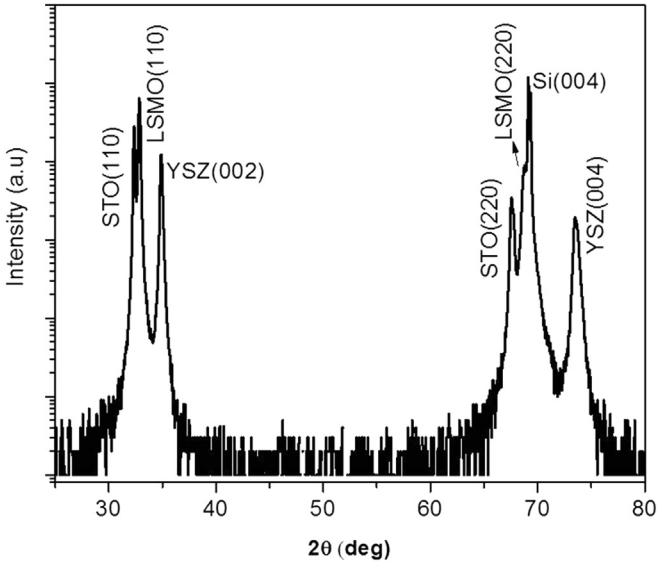

Fig. 1. XRD 2θ scan of LSMO/STO/c-YSZ heterostructure grown on Si (001) substrate.