Microstructural Characterisation of Cuprate / Manganate Films on (110) SrTiO$_3$ Deposited by Laser Ablation

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Abstract. Cross-sectional TEM and microanalysis were carried out to understand at a microscopic level the effects of microstructure and chemistry on the physical properties of manganites and manganite/cuprate films. TEM observations on pure LCMO grown on a (110) STO substrate were carried out first to determine the defect structure and detect any formation of second phase precipitates, as well as microstructural changes not detectable by X-ray reflections. La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) grows epitaxially on a (110) SrTiO$_3$ (STO) substrate. HRTEM reveals a nearly defect-free interface between LCMO and STO with a few irregularly arranged misfit dislocations. The microstructure obtained from laser ablated nanometre scaled La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) / YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) / PrBa$_2$Cu$_3$O$_{7-\delta}$ (PBCO) multilayers on (110) STO was also studied. Diffraction patterns show that all films grow epitaxially on top of the (110) STO substrate, with the c-axis of YBCO in plane. There is a roughness of about 10nm between PBCO and YBCO and the roughness is increased at the YBCO - LCMO interface.

1. Introduction

The magnetotransport properties and colossal magnetoresistance (CMR) of manganites with the perovskite structure have been studied intensively due to their interesting physical phenomena and potential technological interest [1]. The complex structure of orthorhombic LCMO affects its physical properties, such as magnetoresistivity, resistivity and Curie temperature [2 – 4]. Therefore, in this work, the epitaxial behaviour and film quality of pure LCMO on (110) STO was studied. (110) STO can be used to initiate an orthorhombic LCMO crystal lattice growth with the long axis in-plane and short axes at 45° to the plane surface. Spin polarised quasiparticle injection from CMR to a high temperature superconductor has created a lot of interest for spin-injection device technology. Our previous work showed the different magnetoresistance behaviours when the magnetic field was applied parallel and perpendicular to the c-axis of an LCMO/YBCO/PBCO trilayer film on (110) STO [5]. Because of this interesting phenomenon, the microstructure of the trilayer system La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) / YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) / PrBa$_2$Cu$_3$O$_{7-\delta}$ (PBCO) which combined CMR and HTS thin films for spin-injection experiments was then investigated. The PBCO layer was introduced as a buffer layer to produce c-axis in-plane YBCO. Special attention was paid to the interfaces and to the existence of secondary phase precipitation, in order to optimise the properties of this material system.
2. Experimental
All films were grown by pulsed laser deposition with a nominal thickness of ~300 nm onto polished (110) SrTiO₃ substrates at an oxygen pressure of 0.15 mbar. A KrF excimer laser with wavelength 248 nm was used. All layers were deposited at a pulse rate of 5 Hz and an energy density of 0.2 J/cm². The main deposition parameters used were aimed to give high quality single YBCO films on SrTiO₃ (100) as described elsewhere [6]. The tripod technique was used to prepare wedge shaped TEM cross-section specimens in order to avoid sputter etching of the film during ion milling [6]. TEM studies were carried out on a Tecnai F20 operating at 200 kV and equipped with Oxford instruments EDX.

3. Results and Discussion

3.1 Pure LCMO on (110) STO

The basic orthorhombic unit cell (a = 0.5437 nm, b = 0.7679 nm and c = 0.5445 nm [7]) of LCMO will be denoted by subscript o while the LCMO structure referred to as pseudocubic with a = 0.3858 nm [8] is denoted by subscript p. Cross-sectional TEM studies have been employed to investigate the epitaxial behaviour and quality of the pure LCMO film on (110) STO (a = b = c = 0.3905 nm). Figure 1 (a) shows that the as-grown film has a sharp interface with the substrate and flat top surfaces. Misfit dislocations with evident strain contrast are indicated with arrows in figure 1 (a). The SAED patterns in figure 1 (b) are taken from the film and the substrate respectively along the [110] direction of STO. The sharp electron diffraction spots show no satellites or broadening indicating that the films have good single crystallinity. The epitaxial relationship has been found to be <002>LCMO // <110>STO or <110>LCMO // <110> STO. High-resolution, cross-section TEM has demonstrated this epitaxial behaviour as shown in figure 1 (c). The interface is decorated with a few irregularly arranged misfit dislocations. The lattice mismatch calculated based on the lattice parameters is about 1.7 %. The lattice mismatch stress can cause either homogeneous lattice strain or the formation of misfit dislocations at the interface. Most of the misfit dislocations observed are a<100> type, similar to the results reported in [9]. To accommodate fully the misfit, a<100> type misfit dislocations with an average separation of 22 nm are expected. However, the average dislocation separation measured is about ~ 50 nm. This indicates that some of the strain induced by mismatch still remains in the film and that another mechanism (e.g. twin formation) may operate to relax the remaining stress. The LCMO film on (110) STO showed a conventional anisotropy in magnetoresistance when a magnetic field was
applied perpendicular or parallel to the film plane which is similar to the LCMO film grown on (001) STO substrate [10]. EDX was performed on the film matrix and the defect region. The cation concentrations in the matrix and the defect region were similar. This suggested that the defects as indicated in figure 1 a which embedded in the film matrix were differently oriented LCMO grains.

3.2 LCMO/YBCO/PBCO trilayer on (110) STO

A LCMO/YBCO/PBCO trilayer was grown on a (110) STO substrate. Figure 2 shows that the as-grown films have a very good epitaxial relationship: <002_o>LCMO // <110> YBCO // <110> STO, i.e. with the long axis in-plane. The interface between the STO substrate and film is sharp. However, the interface between the layers is not distinguishable in the low magnification image. The trilayer surface is rough, while the pure LCMO layer surface is smooth. The roughness starts at the YBCO / PBCO interface and extends to the YBCO/LCMO interface as shown in figures 3 (a) and (b). The roughness between the YBCO and PBCO is about 10 nm while in the topmost LCMO layer, the roughness of the surface is about 30 nm. Although the interface is not flat, the epitaxial relationship is maintained as indicated by the continuation of (001) YBCO to the (010), LCMO planes (figure 3 (c)).

Figure 2 Cross-sectional TEM image of a trilayer (LCMO/YBCO/PBCO) superlattice including the corresponding diffraction patterns.

Estimated lattice parameters from the HRTEM image suggest that there is an in-plane tensile strain near the interface between YBCO and LCMO. The Curie temperature $T_c$ of the trilayer is about 220K which is lower than the $T_c$ (~250K) of the films grown on a (001) STO substrate. This may be due to the in-plane tensile strain which suppresses the $T_c$ [11]. The magnetisation measurements on the trilayer film are anisotropic as shown in figure 4. The measurements show that when the applied
magnetic field \( (H) \) is perpendicular to the c-direction of YBCO, a simple hysteresis loop is recorded with a coercive field of \( \mu_0H \sim 20 \) mT. When applied along the c-axis, a combination of two hysteresis loops of LCMO is observed. The two hysteresis loops may be related to the existence of two crystallographical phases in the LCMO layer. However, selected area diffraction and EDX measurements show no second phases forming in the LCMO layer, nor is there interdiffusion between the layers. The other reason for the combination phenomenon may be the stress developed in the LCMO layer during growth. The strained lattice induces distortion which can influence the Mn – Mn bonding distance and the Mn – O – Mn bond angle, therefore influencing significantly the magnetic properties [12].

Figure 4 Magnetisation measurements for the LCMO/YBCO/PBCO film with the magnetic field applied parallel and perpendicular to the in-plane c-direction.

References