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Growth and characterization of epitaxial $La_{0.7}Ca_{0.3}MnO_3$ thin films by metal-organic deposition on $(LaAlO_3)_{0.3}$–$(SrAlTaO_6)_{0.7}$ substrates

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Abstract

Thin films of $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) have been grown epitaxially on (001) single-crystal substrates of $(LaAlO_3)_{0.3}$–$(SrAlTaO_6)_{0.7}$ by metal-organic deposition. The microstructures of the LCMO films were investigated by transmission electron microscopy (TEM) on cross-sections. High-resolution TEM observations demonstrated a good quality of epitaxy throughout the entire film thickness. For bolometric application, we calculated the temperature coefficients of resistance (TCR) from the temperature dependence of the resistance. Large value of TCR of approximately 22% at 250 K was obtained for the 80 nm thick film.

Keywords: Thin films; Manganite; Metal-organic deposition; Transmission electron micrsocopy; Temperature coefficient of resistance; Bolometer

1. Introduction

The doped perovskite manganite materials of the type $La_{1-x}Ca_xMnO_3$ (LCMO) have been extensively studied over the past few years, especially in the form of thin films, due to their colossal magnetoresistance (CMR) and then their varieties of applications in magnetic and magnetoresistive devices [1]. In addition to the CMR properties, the LCMO thin films exhibit a large temperature coefficient of resistance [TCR defined as $1/R$ (dR/dT)] close to the resistivity peak (T_p) which makes them promising candidates for infrared imaging sensors based on thermal detectors arrays (bolometer) [2–6]. The physical properties of the manganite thin film are sensitive to structure, oxygen content, and disorder. Therefore, the T_p and resistivity of the film are somewhat different from those of the bulk material [7]. Consequently, the growth method, the deposition parameters, and also the substrate-induced strain will influence the properties. LCMO thin films have been prepared using various techniques such as pulsed laser deposition (PLD), spurting, sol–gel, and molecular beam epitaxy (MBE) [7–11]. In previous papers [12,13], we investigated the epitaxial growth of $La_{0.7}Ca_{0.3}MnO_3$ thin films using the metal-organic deposition (MOD) technique. LCMO thin films with different thicknesses have been grown on (001) single-crystal $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) substrates having different lattices mismatches of (δ=+1.1%) and (δ=−1.81%) with the LCMO, respectively. The microstructures of the LCMO films were found to be dependent on the used substrate, i.e., the lattice mismatch (δ) [14]. On the STO substrate the LCMO film was found to be epitaxially grown with good epitaxy without misfit dislocations or defects throughout all the film thickness. However, for the films grown on LAO substrates, we observed along the LCMO/LAO interfaces misfit dislocations and twins. As well, the TCR properties were found to be dependent on the lattice mismatch. The highly strained films grown on LAO substrates exhibited large TCR which can reach 27.5%/K in comparison with those grown on the STO substrates showing TCR value of approximately 10.2%/K [13]. Therefore, understanding the

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strain is of particular interest since it can be used to advantage in tuning film properties, as has already been demonstrated in cuprates [15]. Thus, in this study we prepared the LCMO films on the very small lattice-mismatched substrate (δ=0.2%) of $(LaAlO_3)_{0.3}$–$(SrAlTaO_6)_{0.7}$ (LSAT). Microstructural study of the LCMO thin films deposited on STO or LAO using different techniques demonstrated a direct correlation between the microstructures of the films and the corresponding substrates [15–18]. So, we observed the obtained films on LSAT substrates using cross-section transmission electron microscopy (XTEM). For the proposed application as IR sensors we calculated the TCR values.

2. Experimental procedure

The starting solution was prepared by mixing the constituent metal-naphthenate solution (Nihon Kagaku Sangyo); it was then diluted with toluene to an appropriate concentration (0.2 mol/l) and viscosity for spin coating. The molar ratios of La, Ca and Mn in the coating solution were 0.7, 0.3 and 1.0, respectively. This solution was spin-coated onto LSAT (001) substrates at 4000 rpm for 10 s. To eliminate the toluene, the metal-organic (MO) film was then dried in air at 100 °C for 30 min. Before the final annealing, a preheating step at 500 °C for 30 min is necessary to decompose the organic part. This preheating step is also required to prevent the formation of fissures on the film surface during the final annealing at high temperature. To obtain a satisfactory film thickness for bolometric applications, the above procedure (coating, drying, and preheating) was repeated several times (up to 4 times) giving rise to a corresponding number of superimposed layers in the LCMO product film. The final annealing was carried out in a conventional furnace at 1000 °C for 60 min in air.

The cross-section transmission electron microscopy (XTEM) observations were performed using a high resolution electron Hitachi H-9000 microscope operated at 300 kV. The XTEM specimens were prepared following the conventional method, i.e., mechanical cutting, face-to-face gluing, mechanical grinding, polishing and dimpling, followed by Ar-ion milling at 4 kV. The surface morphology and roughness of the samples were studied by atomic force microscopy (AFM: Nanopics 2100) with the damping mode. The resistance–temperature $R/R_{300}-T$ (R_{300}: resistance value at 300 K) curves were measured by the conventional DC four-probe method and by cooling the samples from 320 K to liquid nitrogen temperature (77 K).

3. Results and discussion

3.1. XTEM structure of the films

Fig. 1 shows a cross-section TEM image (a) and the corresponding selected area electron diffraction pattern (SAED) (b) of the 2-layers LCMO film grown by MOD process using a thermal annealing at 1000 °C on LSAT substrate. It can be seen that the LCMO film thickness is approximately of 40 nm. Therefore, one deposited layer by MOD process is 20 nm thick. Since, the film resulted from the deposition of two layers; we expected the presence of a kind of interface separating the two deposits as already observed in indium tin oxide prepared by sol–gel process [19]. Nevertheless, as can be seen in the cross-section TEM image [Fig. 1(a)], the film exhibited an excellent homogeneity in depth without interface or defects. The SAED pattern (Fig. 1(b)) demonstrated the (100) single crystalline structure of the LCMO film.

The lattice mismatch between the LCMO film and the substrate can be accommodated either by straining the lattices or by the formation of misfit dislocations at the interface depending on the elastic properties of the material and the film thickness [15]. The lattice mismatches with the LSAT and STO substrates are small resulting in a biaxial tensile strain of 0.2% and 1.1%, respectively. The lattice mismatch with LAO, however, is rather larger with a compressive strain of −1.81%. Microstructural properties of the LCMO films grown on STO and LAO substrates were reported in details elsewhere [13]. The SAED patterns and high-resolution TEM images demonstrated the epitaxial growth of the LCMO on both STO and LAO substrates. For the film grown on LSAT substrate, HRTEM images taken at the top part of the LCMO film (Fig. 2(a)), the middle part (Fig. 2(b)) and the interface (Fig. 2(c)) demonstrate

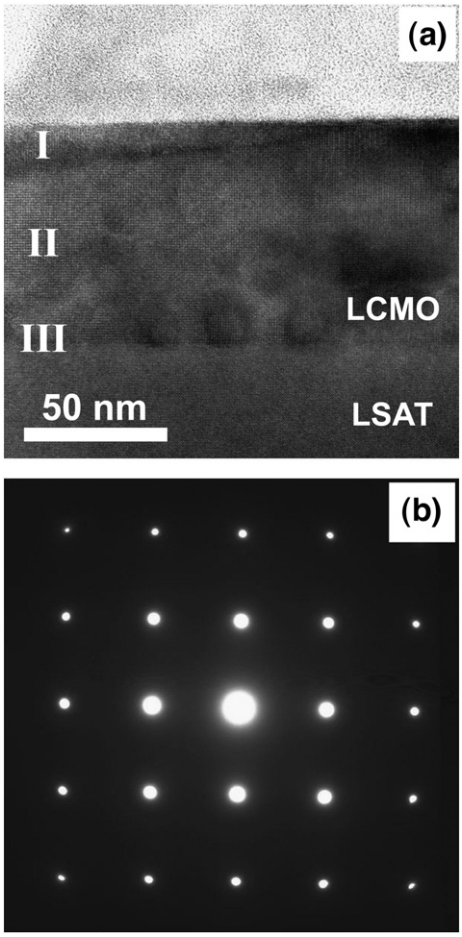

Fig. 1. (a) cross-section TEM image and (b) SAED pattern of the LCMO thin film grown on LSAT substrate.