Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2007) 6527–6530
applied surface science
www.elsevier.com/locate/apsusc

Pulsed-laser crystallization and epitaxial growth of metal–organic films of Ca-doped $LaMnO_3$ on STO and LSAT substrates

K. Daoudi *, T. Tsuchiya, T. Kumagai

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, 305-8565 Tsukuba, Japan

Available online 23 January 2007

Abstract

Ca-doped $LaMnO_3$ (LCMO) thin films have been successfully prepared on $SrTiO_3$ (STO) and $[(LaAlO_3)_{0.3}$–$(SrAlTaO_6)_{0.7}]$ (LSAT) substrates using the excimer laser assisted metal–organic deposition (ELAMOD) process. The crystallization and the epitaxial growth of the amorphous metal–organic LCMO thin films have been achieved using a KrF excimer laser irradiation while the substrates were kept at constant temperature of 500 °C. Epitaxial films were obtained using laser fluence in the interval of 50–120 mJ/cm^2. The microstructure of the LCMO films was studied using cross-section transmission electron microscopy. High quality of LCMO films having smooth surfaces and sharp interfaces were obtained on both the STO and the LSAT substrates. The effect of the laser fluence on the temperature coefficient of resistance (TCR) was investigated. The largest values of TCR of the LCMO grown on the LSAT and the STO substrates of 8.3% K^{-1} and 7.46% K^{-1} were obtained at different laser fluence of 80 mJ/cm^2 and 70 mJ/cm^2, respectively.

PACS : 81.15.−z; 81.15.Np; 73.61.−r; 71.30.+h

Keywords: LCMO; Excimer laser; MOD; TEM; TCR; Bolometer

1. Introduction

Lanthanum manganese oxides have been widely investigated in recent years in view of potential technological applications in read head memory, spin sensitive devices, and infrared bolometric applications [1–4]. Presently, these manganites in thin film form have been mainly investigated using the molecular beam epitaxy (MBE) [5], pulsed laser deposition (PLD) [6], and sputtering [7]. Using these techniques, high vacuum and post-annealing at high temperature are required to obtain epitaxial films with satisfactory magnetic and electrical properties for the desired applications. While these techniques have demonstrated growth of device quality material, the microelectronic technology has an increase demand for higher integration. The reductions of the substrate temperature, or of the processing time, are desirable in order to minimize impurity diffusion and to avoid junction destruction. In this context, pulsed-laser assisted epitaxy of various materials was proposed at the end of the 1980s. More recently, the excimer laser assisted to chemical processes such: sol–gel [8], chemical vapor deposition [9] or the metal–organic deposition (MOD) [10] have been considered promising alternatives for thin film processing at low temperature. Among these processes, the MOD is distinguished especially for the epitaxial growth of various functional oxides materials in thin film form [11,12]. Instead of the thermal annealing at high temperature (over 700 °C), an excimer laser irradiation at room temperature or at a relatively low temperature was found to be sufficient to crystallize the starting metalorganic compounds [10]. Already epitaxial $Pb(Zr,Ti)O_3$ (PZT) [13], $La_{1-x}Sr_xMnO_3$ (LSMO) [14], $La_{1-x}Ca_xMnO_3$ (LCMO) [15,16] and SnO_2 [17] have been epitaxially grown on various single-crystal substrates using the excimer laser assisted metalorganic deposition (ELAMOD) process. Understanding the formation mechanism of an epitaxial oxide thin film using the ELAMOD process is of particular interest since it can be used to advantage in tuning film properties. Therefore, in this paper we prepared LCMO thin films on different lattice-mismatched substrates STO and LSAT. The microstructural properties of the obtained films were examined in details using high resolution transmission

* Corresponding author. Tel.: +81 29 861 3442; fax: +81 29 861 3442.
E-mail address: kais.daoudi@gmail.com (K. Daoudi).

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.01.033

electron microscopy (HRTEM). The LCMO thin films were known to exhibit large temperature coefficient of resistance (TCR = $1/R(dR/dT)$) which makes them ideal candidates for uncooled or moderately cooled infrared sensors (bolometer) [18]. So, we studied the effects of the laser fluence on the TCR properties of the LCMO films on both LSAT and STO substrates.

2. Experimental

The starting solution was prepared by mixing the constituent metal–naphthenate solution (Nihon Kagaku Sangyo) and diluting with toluene to obtain the required concentration and viscosity. 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 (4000 rpm, 10 s) onto STO and LSAT (0 0 1) single-crystal substrates. To eliminate the toluene, the metal–organic (MO) film was then dried in air at 100 °C for 10 min. To start the metal–organic decomposition and to prevent film degradation during laser irradiation, a pre-heating step at 500 °C for 10 min has been found necessary. A 248 nm KrF excimer laser (Lambda Physik, Compex 110) was focused through a homogenizer on a film surface of 0.57 cm^2. The pulse duration was about 20 ns and a repetition rate was set constant at 10 Hz. The substrate temperature during the laser irradiation is maintained at 500 °C. To adjust the film thickness, these operations (coating, drying, preheating and irradiation) are repeated two times.

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 resistance–temperature R/R_{300}–T (R_{300}: resistance value at 300 K) curves were measured by the usual DC four-probe method and by cooling the samples from 320 K to liquid nitrogen temperature (77 K).

3. Results and discussion

3.1. Microstructure of the LCMO films

Fig. 1 shows a low magnification cross-section TEM image (a), the corresponding selected area electron diffraction (SAED) pattern (b), and a HRTEM image showing details at the interface (c) of the LCMO film grown on the LSAT substrate. The LCMO film is composed of two layers (coating, drying, preheating and irradiation); each one was irradiated during 60 min with a laser fluence of 80 mJ/cm^2 while the substrate was kept at constant temperature of 500 °C. The total film thickness is precisely measured from the XTEM image (Fig. 1(a)) and is approximately of 40 nm. Since the LCMO film is formed by two supperimposed layers, we expect the presence of interface between the layers, as already observed in multilayred indium tin oxide films prepared by the sol–gel process [19,20]. As can be seen in Fig. 1(a), the film exhibit

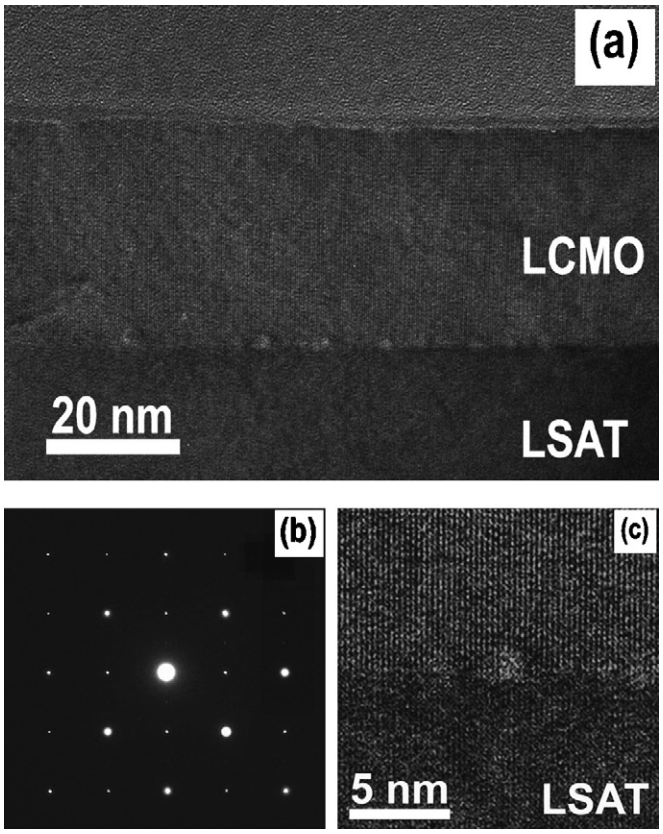

Fig. 1. (a) XTEM image, (b) SAED pattern and (c) HRTEM image of the LCMO film grown on the LSAT substrate using the ELAMOD process with a KrF laser at a fluence of 80 mJ/cm^2, a repetition rate of 10 Hz, an irradiation time of 60 min and a substrate temperature of 500 °C.

good homogeneity in depth without interface between the layers or granular structures. As well, the LCMO/LSAT interface is sharp, suggesting that no atomic migration takes place during the growth process. The SAED pattern (Fig. 1(b)) and the HRTEM image (Fig. 1(c)) indicates a perfect ''cub-on-cub'' epitaxy of the LCMO film on the LSAT substrate. This result is expected since the lattice mismatch between the LCMO film and the LSAT substrate is small as 0.1%. Similar microstructural features were observed for the LCMO film grown on the STO substrate at the same preparations conditions (Fig. 2). The film grown on the STO substrate is also composed of two layers. The film thickness is approximately of 40 nm (Fig. 2(a)) which is equal to that of the film grown on the LSAT substrate. Therefore, using the ELAMOD process one LCMO deposited layer is approximately of 20 nm which is independent of the substrate material. The HRTEM image (Fig. 2(c)) evidences a perfect epitaxial quality of the LCMO film in the region close to the LCMO/STO interface which is sharp. Both LCMO films grown on STO and LSAT substrates present a flat surface indicating a very low roughness. This result is in agreement with our previous atomic force microscopy (AFM) measurements [17].

3.2. TCR properties

In Fig. 3(a), there are shown the $R(T)$ curves of the LCMO thin films grown on the LSAT and the STO substrates. The