Journal of Science and Healthcare Exploration (JSHE) ISSN(O): 2581-8473
Monthly, Peer-Reviewed, Refereed, Indexed Journal [Impact Factor : 5.273]
Volume - 6, Issue - 10, October – 2024

DOIs:10.2019/JSHE/JSHE202410001 --:-- Research Paper / Article / Review

Surface Morphological Study of CSD Grown CMR Manganite Thin Films Through Atomic Force Microscopy

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Abstract: *Thin films are mostly prepared by various techniques like PLD, Sputtering, sol-gel, MOCVD, LMBE etc. We have prepared the manganite thin films of* $La_{0.7}Sr_{0.3}MnO_3$ *(LSMO) of various thicknesses viz. 75 nm, 150 nm, 225 nm, 300 nm. Thin films were deposited by a special technique known as Chemical Solution Deposition (CSD) using automated spin coater unit on the (h00) – oriented single crystalline* $LaAlO_3$ *(LAO) substrate and then subsequent heat treatments were given. Desired film thickness was achieved via control of the number of deposition sequences. X-ray diffraction (XRD) study shows that all the LSMO films have the cubic structure and highly epitaxial (h00) – oriented growth was observed on LAO (h00) substrate. As the film thickness increases, increase in lattice parameter was seen. Surface Morphological Study was carried out through Atomic Force Microscopy (AFM). RMS roughness and grain size were calculated through AFM images. As the film thickness increases, grain size and RMS roughness also found to increase.*

Keywords: *Manganites, Chemical solution deposition, colossal magnetoresistance.*

1. INTRODUCTION:

The correlation of the electronic and magnetic properties of colossal magnetoresistance (CMR) materials with structural properties has been a topic of enormous research activity over the last few years. This family of perovskite oxides having the general chemical formula $Re_{1-x}A_xMnO_3$ (where Re is a rare earth element, A = Sr, Ca, Ba, Pb etc.) exhibits large changes in resistance under the application of a magnetic field [1]. CMR in these materials refers to the change in magnitude of the resistivity near T_c upon the application of magnetic field which makes them attractive candidates for the application of magnetic field sensing and magnetic recording devices. One of the most widely researched area in this field is the growth of high quality material with T_c at room temperature. The magnetic and electrical properties of the films of these CMR oxides are very sensitive to the material processing parameters, such as the method of deposition, the temperature of growth [2], post-deposition annealing treatment [3], quality of epitaxy and mismatch with the substrate [4]. Strain and microstructure play important role in determination of the physical properties of films.

In general, thin films of CMR manganites are prepared by PLD [5], metalloorganic chemical vapour deposition (MOCVD) [6], or high pressure magnetron sputtering [7]. These methods of physical or chemical deposition have their respective advantages and disadvantages. All these methods, however, are infrastructure intensive. The physical vapor deposition methods give good films with proper deposition condition but are not suitable for uniformly over a large area. While MOCVD capable of giving rise to large area films, needs precursors that are difficult to handle and can be hazardous. An alternate method of large area growth is to use wet chemical routes such as Chemical Solution Deposition (CSD) or the sol-gel route [8]. In general, CSD methods have been used for the growth of ferroelectric titanate films. There are reports on the growth of thin films of CMR manganites by wet chemical methods such as sol-gel or the CSD route [2, 9, 10]. The main advantages of the CSD route are - (i) it is easy to control the composition of such compounds by changing the stoichiometric ratio of the starting material and it can ensure high homogeneity, (ii) it has a relatively low processing temperature, and it does not take a long time to prepare; also, the fabrication of large area thin films is possible and (iii) it is cost effective. This method also has the advantage of quick prototyping so that a large number of film compositions can be quickly tested in a cost- effective manner.

A common problem of the CSD method, however, is the low quality of films, which is sometimes obtained by this growth method. In particular, they have very low T_c or T_p (where the resistivity peaks at the onset of ferromagnetic transition) and rather high resistivity, p. It is reported that these problems are not generic to the chemical route. These problems can arise because of a number of reasons, like the use of improper substrate, unoptimized growth condition and uncontrolled grain morphology [11]. These problems can even arise in more sophisticated growth process like PLD, MBE or MOCVD. Understanding the role of strain and microstructure on the magnetism and transport is a necessary step in elucidating the origin of the CMR in this class of materials. The strain state and microstructure vary as a function of film thickness in a single thin film sample. Atomic scale roughness of thin films has a great importance from a fundamental point of view as well as for application perspectives. Surface roughness strongly affects the magnetic properties, thermal conductivity, thermal stability etc. of thin films. The main motivation of these efforts is to develop the good quality of thin films by the simplest, low cost CSD technique and study its microstructure and roughness properties with varying film thickness.

2. EXPERIMENTAL:

Polycrystalline thin films of LSMO were prepared by the CSD technique. The flow chart diagram in Figure 1 illustrates the precursor solution preparation, heating and deposition steps. The solution of three component oxide was prepared from Lanthanum (III) acetate hydrate, Strontium acetate and Manganese (II) acetate tetrahydrate of high purity (Sigma Aldrich). Each was dissolved in a solution of distilled water and acetic acid in stoichiometric amount to make films with the composition $La_{0.7}Sr_{0.3}MnO_3$. The optimum ratio of water to acetic acid was 1:1 (v/v). The concentration of the solution was 0.4 M. To get a good wet ability of the substrates, one side polished LAO (*h00*) substrates (Crystal GmbH, Germany) were cleaned sequentially using deionized water, acetone and trichloroethylene for 20 minutes and then dried in an oven. The films were prepared by spin coating of clear solution with no undissolved components on LAO substrate. To obtain clear solution, it was heated at 80° C - 90° C. Each spin coating cycle lasted 20s at 6000 rpm for the LSMO-1 (one layer coating), LSMO-2 (two layers coating), LSMO-3 (three layers coating), LSMO-4 (four layers coating) compositions used give ≈ 75 nm thickness. Each spin coating cycle was followed by drying at 120º C and pyrolysis at 350º C for 30 min. After the final deposition, the films were annealed at 1000º C for 12 h in flowing O_2 atmosphere using programmable tube furnace. Heating rate 2 °C/min and cooling rate 1 °C/min were maintained during annealing process. X-ray diffraction (XRD) was utilized for the confirmation of the phase formation as well as the orientation of the film. The surface morphological study was carried out through Atomic Force Microscopy (AFM). RMS roughness and grain size were calculated through AFM images.

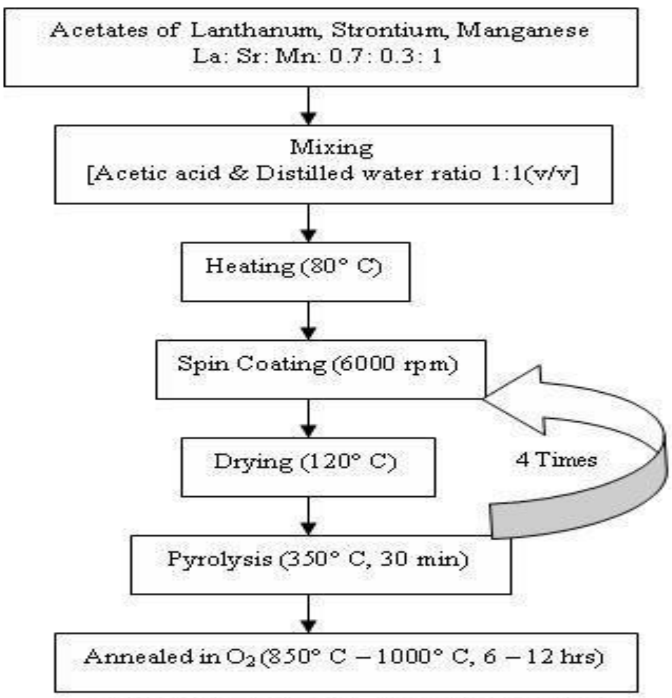

Figure 1: Flow diagram of Chemical Solution Deposition Technique.

3. RESULTS AND DISCUSSION:

The structural characterization was carried out employing XRD (Siemens Diffractometer, UGC-DAE CSR, Indore) and typical indexed XRD patterns are shown in Figure 2. The analysis of the XRD data revels that the films are polycrystalline and all have a cubic structure with lattice parameters as listed in Table 1. The XRD measurements confirm the epitaxial growth of (h00) - oriented LSMO films. X-ray-diffraction patterns show that the films are of high quality and single phase without any extra impurity peaks. Lattice parameter has been found to increase with the film thickness.

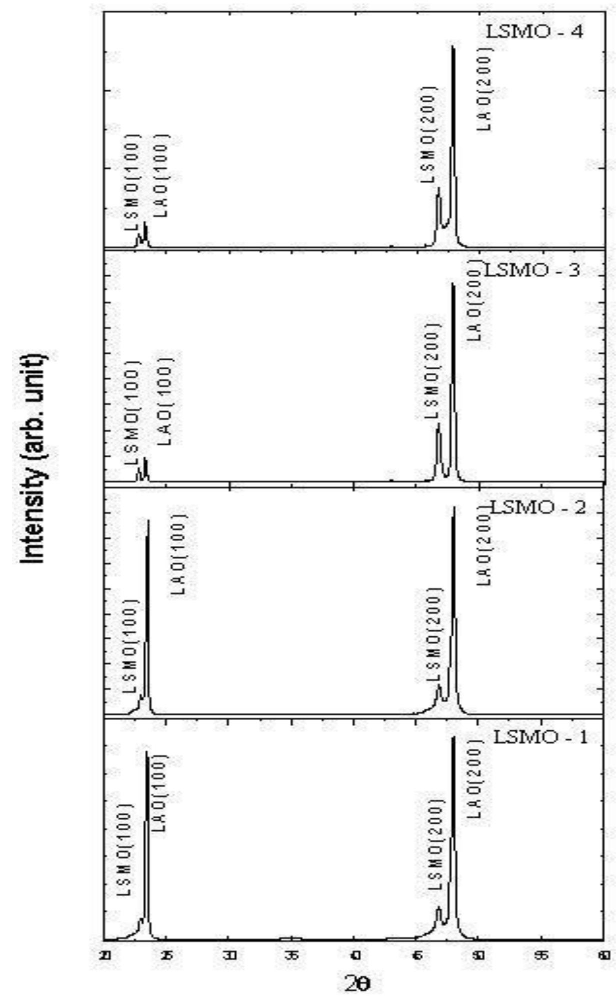

Figure 2. Indexed XRD patterns of LSMO-1, LSMO-2, LSMO-3, LSMO-4 thin films on LAO substrate.

The particle sizes of the LSMO films were estimated by using the Scherrer formula [12]: $d = 0.9\ \text{ß} / D\cos\theta$, where d is the particle size, ß - the X-ray wavelength used, D - the peak full-width at half-maximum (FWHM), and θ - the Bragg angle. We observe increment in particle size as thin film thickness increases as shown in Table 1. The substrate plays a crucial role in the structural properties of the LSMO materials. The most commonly used single crystalline substrates for CMR manganites are $SrTiO_3$ (STO, a = 0.3905 nm, cubic), $LaAlO_3$ (LAO, a = 0.3788 nm, cubic), MgO (a = 0.4205 nm, cubic) and $NdGaO_3$ (NGO, orthorhombic with a = 0.5426 nm, b = 0.5502 nm and c = 0.7706 nm). The lattice mismatch δ along the interface is defined by $\delta = (a_{p\ substrate} - a_{p\ bulk})/a_{p\ substrate}$. If $a_{p\ substrate} > a_{p\ bulk}$, positive values of mismatch correspond to tensile strains which indicate that the cell is elongated in the film's plane and compressed along the out- plane growth direction. If $a_{p\ bulk} > a_{p\ substrate}$, negative values of mismatch correspond to compressive stresses which indicate that the cell is elongated along the growth direction and compressed in the film's plane [13]. In case of LSMO film, the lattice mismatch between LSMO and Substrate is negative (Table 1) leads to compressive stress in the epitaxial films.

Thin film	Thickness (nm)	Cubic Lattice Parameter (Å)	Lattice Mismatch (δ%)	Particle Size (Scherrer Formula) (nm)	Grain Size (AFM) (nm)	RMS Roughness (AFM) (nm)
LSMO-1	75	3.872	-2.22	27	~30	7 11
LSMO-2	150	3.880	-2.42	35	~38	8 9
LSMO-3	225	3.891	-2.72	45	~43	9 8
LSMO-4	300	3.894	-2.80	48	~51	11 7

Table 1: The values of film thickness, cubic lattice parameter, lattice mismatch, particle size (Scherrer formula), grain size (AFM), RMS roughness for LSMO thin films.

The grain morphology was probed with an Atomic Force Microscopy (AFM). The LSMO films of various thicknesses are composed of uniformly distributed grains and the larger grains grew with increasing thickness of the film. Film thickness, average grain size and surface roughness calculated from AFM images are shown in Table 1. As the film thickness increases, average grain size and surface roughness increase. It is also noted that the crystalline quality of LSMO improves as the film thickness increases, while the surface becomes more rougher. This may be due to the deviation of the lattice parameter for LSMO and Substrate which results in the compressive stress.

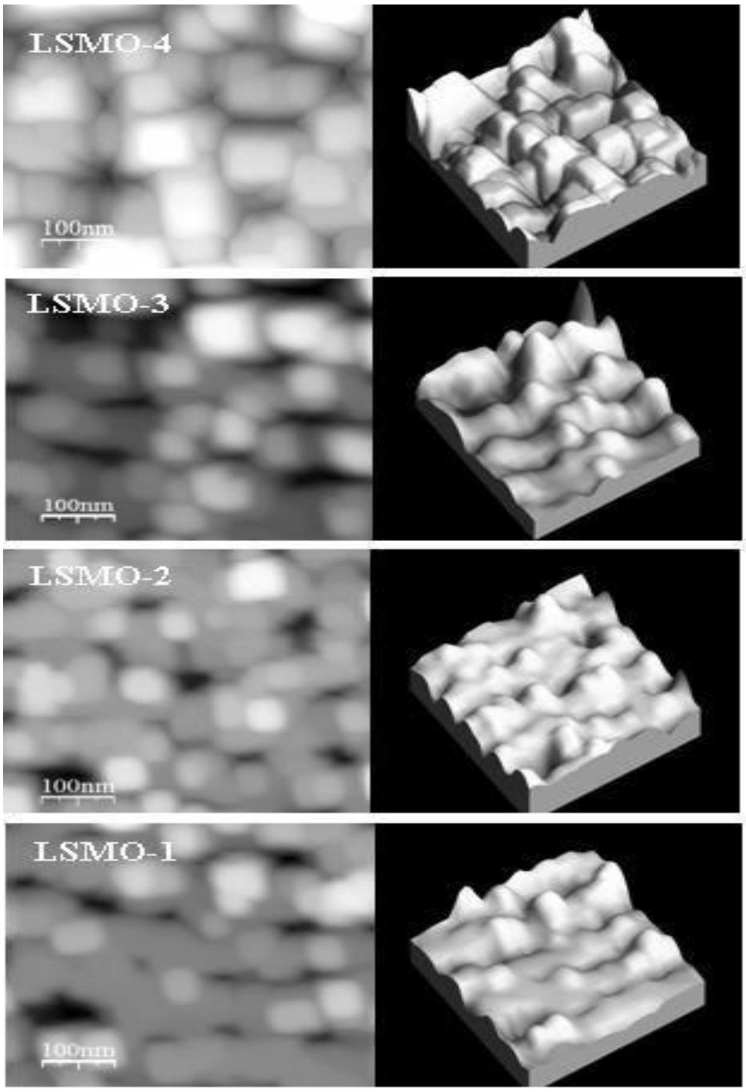

Figure 3 : AFM images of LSMO thin films with their respective 3D view.

4. CONCLUSION:

XRD patterns confirm the high quality, single phase in nature and highly epitaxial (*h00*) – oriented growth of the films. The lattice parameter increases as the film thickness increases and are found close to the lattice parameter of bulk sample for higher thicknesses. The negative value of lattice mismatch between LSMO and Substrate leads to compressive stress in our epitaxial films of LSMO. Grain sizes obtained from AFM images are found increasing with the annealing temperature is the common phenomenon but we observed increment in grain size with film thickness. Slight increment in RMS roughness was also observed with film thickness.

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