Sol-Gel Derived $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Films by Pulsed Laser Deposition

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Abstract: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) nanocomposite was synthesized using sol gel method at 600 °C. The structure and elemental analysis were confirmed by X-ray diffraction (XRD) and energy dispersive X-Ray (EDX) respectively with rhombohedral crystal structure. High resolution transmission electron microscope (HR-TEM) imaging showed that the prepared LSM has uniform shape with particle sizes ranging between 5 and 95 nm, and lattice fringes also displayed the rhombohedral structure. Thin films of LSM with 97 nm were deposited on clean Si (100) single crystal substrate by PLD using Nd:YAG (1,064 nm) with 10 Hz repetition rate and 6 ns pulse duration at room temperature in high vacuum of $\sim 6 \times 10^{-6}$ torr. LSM films were annealed at temperatures of 400, 600, 800 and 1,000 °C for 2 h. The XRD indicated that crystallization is enhanced by increasing annealing temperature. Additionally, grain size was increased by rising annealing temperature as indicated from field emission scanning electron microscope (FESEM) imaging. The average roughness (R_a) and root mean square roughness (R_q) were decreased by increasing annealing temperature up to 600 °C then increased by further temperature increasing as showed by atomic force microscope (AFM) images. Raman spectra were recorded in wave numbers 100-1,000 cm^{-1} and all major peaks appeared at annealing temperature 1,000 °C.

Key words: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM), pulsed laser deposition (PLD), thin films, annealing, Raman spectroscopy.

1. Introduction

In recent years perovskite manganite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) is interesting material for most technological devices such as for cathode in solid oxide fuel cell cells (SOFC) [1]. LSM has good electrocatalytic in SOFC operation and also stable in hot oxidant atmospheres. In the LSM structure, strontium atoms replace lanthanum atoms, which are coordinated by twelve oxygen atoms. Sr^{2+} doping play an important role in electronic conductivity and chemical stability against yttria stabilized zirconia (YSZ), the most commonly electrolyte for SOFC. The amount of Sr must be carefully chosen because it can deform other properties, such as enlarging the thermal expansion coefficient. The normal doping amount of strontium is among 10 and 30 mol% [2]. The LSM can be stabilized in rhombohedral, orthorhombic and

mixture of both phases [3]. Sol-gel method was used for synthesis LSM in the form of powder with small particle size using citric acid as polymerizing agent and ethylene glycol taking in consideration the variation of pH. Besides the synthesis parameters, further heat treatment is also an important step because the powder obtained contain a large amount of organic material so must be heated to obtain pure LSM, also it can modify the crystal structure [4].

A possible approach to improve the quality of thin films is to use pulsed laser deposition (PLD). PLD is a thin film deposition technique, which has been used to fabricate a wide range of materials [5]. PLD produces energetic species, which results in the increase of the sticking coefficients and adatom surface mobility, enhancing epitaxy [6]. This technique consists in the deposition of a material on a substrate inside a vacuum chamber by focusing a high power pulsed laser beam that strikes a target composed of the

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elements that are to be deposited. The transfer of the material from the target to the substrate enables the direct deposition of complex multi element oxides. PLD offers the ability to produce materials that are not possible under thermal equilibrium conditions. Deposition occurs in short pulses resulting in a high deposition flux typically several orders of magnitude larger than the steady-state flux in Molecular beam epitaxy (MBE). Indeed, the average growth speed for PLD is limited only by the repetition rate of the laser. Thus, PLD technique can perform a variety of fundamental kinetic studies, which are difficult to be achieved by using MBE technique [7]. The aim of this study is to prepared LSM powder using sol gel method. Powder of LSM was used as a target material after characterized by X-ray diffraction (XRD), High resolution transmission electron microscope (HR-TEM), Energy dispersive X- Ray(EDX) and particle size distribution (PSD) to fabricate thin films deposited on Si (100) single crystal using PLD technique. The film structure and morphology are characterized by (XRD), Field Emission Scanning Electron Microscope (FESEM), atomic force microscope (AFM) and Raman spectroscopy at different annealing Temperatures.

2. Experimental

2.1 Preparation of LSM Powder

LSM powder was prepared by sol gel method as follows. 0.7 mol of $\text{La}(\text{NO}_3)_3$ (99.0%, Alpha Chemika, India) and 0.3 mol of $\text{Sr}(\text{NO}_3)_2$ (99.99%, Junsei Chemical, Japan) as source of (La) and (Sr) into 40 ml ethylene glycol were stirred until dissolved, Addition of 1.0 mol of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%, Alpha Chemika, India) as (Mn) source with 4 g from citric acid were added into the solution until mixed. The pH adjust to 1 using pH meter. The mixture stirred in the temperature range 100-150 °C until the gel formed after that the gel was calcinated at temperature 600 °C for 5 h [8]. The prepared LSM powder was subjected to XRD analysis (Panalytical –

Empyrean, Netherlands) Equipped with CuK α Radiation $\alpha = 1.5406 \text{ \AA}$. Scanning rate 0.1° in the 2θ range from 20-70°, step time = 1 sec. HR-TEM was conducted at 200 kV and (EDX) then compressed into pellet of diameter 0.7 cm at 40 Mpa pressure.

2.2 Preparation of LSM Thin Films

Thin films of LSM were fabricated using PLD (Nd: YAG laser) with wave length 1,064 nm, 10 Hz repetition rate and 6 ns pulse duration was used. The laser energy was fixed at 120 mJ/pulse. The average thickness of the films was 97 nm using ZYGO Maxim-GP 200 profilometer. The target to substrate distance was fixed at 4.5 cm. The pressure in the chamber was held constant high vacuum of $\sim 6 \times 10^{-6}$ torr, during the deposition for 15 min on Si (100) single crystal substrate. Si (100) was cleaned before deposition using acetone, ethanol and ultrasonic. The as-deposited thin films were annealed at 400, 600, 800 and 1,000 °C for 2 h in air to obtain the perovskite phase. The thin films were characterized by XRD, FESEM, Raman spectroscopy and AFM.

3. Results and Discussion

The structure and phase purity of LSM target was examined by XRD measurements as shown in Fig. 1. The XRD patterns reveal the LSM target is in single phase based on card (PDF#04-012-5784) with rhombohedral structure of space group (R-3C). The prepared LSM target showed peaks at (012), (110), (202) (024), (122), (018), (220), (036) and (134). The crystalline size was calculated using the well-known Scherrer formula [9]:

$$\text{Crystalline size } (D) = \frac{0.9\lambda}{B \cdot \cos\theta} \quad (1)$$

where, λ is the X- ray wavelength and equals 1.5406 Å, B is full width at half maximum intensity (FWHM) in radian. θ is Bragg angle. For plane (110) FWHM equals 0.1968 and $2\theta = 32.67^\circ$ lead to $D(110) = 46 \text{ nm}$ (HR-TEM) of LSM target show relatively spherical shape with narrow distribution, particles highly bonded to each other as agglomeration and particle sizes

Fig. 1 XRD of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ target.

in the range of 5-95 nm as in Fig. 2a. The inset indicated selected area electron diffraction (SAED) pattern of LSM and the lattice fringes also display the rhombohedral structure of polycrystalline LSM.

The particle size measured from HR-TEM and PSD is always larger than the average crystalline grain size calculated from the XRD, because the agglomerated particles included several crystalline grains in accordance with result described by S. Daengsakul *et al* [11]. EDX spectra confirms the presence of Lanthanum, Strontium, Manganese and Oxygen in the synthesized perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. This is good evidence that the synthesized nanocomposite of the proposed structure are in proper stoichiometry and no other peak related to any impurity has been assigned in the EDX in which the copper and carbon peaks related to the grid of EDX device.

X-ray diffraction of the as deposited LSM films in Fig. 3 and LSM films annealed at different temperatures which indicates that the as deposited film and film annealed at 400 °C were in amorphous nature and no diffraction peaks appeared. The diffraction peak at $2\theta = 32.427^\circ$ corresponding to the

(110) peak of LSM based on card (PDF# 04-014-7256) indicates the film crystallizes at temperatures between 600 and 1,000 °C. Also the (110) peak enhanced after increase annealing temperature up to 800 °C. The crystallinity become well and most of peaks appear at 1,000 °C and have the same structure as target, but the other peaks of LSM film on Si regardless (110) plane as in Fig. 3 not clear because the thickness is very thin compared to target this agree as mentioned in Ref. [10]. The (110) peak shifts toward low-angle direction at annealing temperature 800 °C, attributed to the lattice constant increases because of Mn^{4+} ionic changing to Mn^{3+} and this in accordance with Ref. [12] and also higher temperature.

3D of AFM $2\ \mu\text{m} \times 2\ \mu\text{m}$ scan area were performed using in contact mode using nonconductive silicon nitride. There are columnar growth like island due to lattice mismatch between the LSM film and Si (100) substrate, which is given by:

$$\delta\% = \frac{a_{\text{substrate}} - a_{\text{film}}}{a_{\text{substrate}}} \times 100 \quad (2)$$

where a lattice constant and has a value for Si (100) substrate and LSM film equals 5.4037 and 5.5328 Å

(a)

(b)

Fig. 2 (a) HR-TEM of LSM target and the inset (SAED), (b) EDX of LSM target and (c) PSD of LSM target.

Fig. 3 XRD of the (a) as deposited LSM film and films annealed at temperature of (b) 400 °C, (c) 600 °C (d) 800 °C and (e) 1,000 °C.

respectively lead to the lattice mismatch $\delta = -2.38\%$. Average roughness (R_a), root mean square roughness (R_q) and mean height were changed according to annealing temperature as in Table 1 and it was found the average roughness and root mean square roughness found to be decrease from the as deposited film (Fig. 4a) up to film annealed at 600 °C (Fig. 4c)

and the surface become smooth at 600 and 800 °C (Fig. 4d) then R_a and R_q were increased at 800 °C and 1,000 °C (Fig. 4e) due to increase in mean height as indicated from Fig. 4f according to Eq. (3) in addition to the grain size was increased due to annealing where incase of as deposited film and film annealed at 400 °C were in amorphous nature as confirmed by XRD (Fig. 3),

Table 1 AFM parameters.

AFM parameters	As deposited film	400 °C	600 °C	800 °C	1,000 °C
R_a (nm)	181.1	132.3	97.04	114.5	233.7
R_q (nm)	226.2	170.5	136.0	154.7	290.6
Z (nm)	500.1	465.8	231.8	362.5	593.2

Fig. 4 AFM of the (a) as deposited film and films annealed at different temperatures (b) 400 °C (c) 600 °C (d) 800 °C (e) 1,000 °C (f) R_a and R_q versus temperature.

so the grain are distribute randomly and surface become poor homogeneity and mean height high compared to annealed films at 600 and 800 °C. So the film annealed at 600 °C is better film with homogenous and smooth surface. The relation between root mean square roughness, average roughness and mean height Z as in Eq. (3) [13].

$$R_{rms} = \sqrt{\frac{\sum_{n=1}^Z (Z_n - Z)^2}{N-1}} \quad (3)$$

where, Z_n is the height of nth data, Z is the mean height of Z_n and N is the number of data.

It was shown from FESEM that the particles are spherical and the grain size increase as increasing

annealing temperature and as shown in Fig. 4. Because annealing the LSM films in air result in saturation of oxygen bonds and removal of

mechanical stresses as result the grain size increase [14]. The microstructure of the film has cracks at annealing temperature 1,000 °C as shown in Fig. 4e,

Fig. 5 FESEM of LSM thin films (a) as deposited film, (b) film annealed at 400 °C, (c) film annealed at 600 °C, (d) film annealed at 800 °C and (e) film annealed at 1,000 °C.

Fig. 6 Raman scattering of LSM thin films of 97 nm thickness assigned by (*) deposited on Si (100) single crystal at different annealing temperature using He-Ne laser with 532 nm wavelength in the wave number range from 20-1,000 cm^{-1} and the laser power 10 mW. The strong feature at 520 cm^{-1} is the peak of Si (100): (a) as deposited and films annealed at (b) 400 °C (c) 600 °C, (d) 800 °C and (e) 1,000 °C.

Table 2 Assignments of the bands observed from the Raman spectra of the as-grown and annealed LSM thin films at different temperatures.

As deposited film (cm^{-1})	Annealed at 400 °C (cm^{-1})	Annealed at 600 °C (cm^{-1})	Annealed at 800 °C (cm^{-1})	Annealed at 1,000 °C (cm^{-1})	Vibrational assignment
-	-	120.25	-	112.36	A_{1g} phonon signal
-	-	-	-	145.27	A_{1g} phonon signal
-	-	-	163.95	177.27	A_{1g} phonon signal
-	-	-	-	212.53	A_{1g} phonon signal
-	-	-	-	257.43	A_{1g} phonon signal
301	303.15	-	-	329.06	MnO_6 stretching $\text{Mn}^{3+}\text{-O-Mn}^{4+}$
-	-	-	467.66	459.81	Stretching of MnO_6
-	-	-	-	492.06	A_g JT mode (Jahn Teller)
519.58	520.18	520.18	519.07	522.00	Si (100)
-	-	-	589.52	596.12	A_g JT mode (Jahn Teller)
620.11	-	620.06	-	-	MnO_6 stretching mode
-	645.11	-	-	-	B_{2g} breathing mode + MnO_6 stretching mode
-	659.20	-	658.10	664.50	B_{2g} breathing mode+ bending of MnO_6

due to different in thermal expansion coefficient between LSM and Si (100) as mentioned in Ref. [10]. The bigger particles in FESEM come from the target as a result of micro cracks and weakly attached particles. Also superheated of the surface region of LSM films reaches higher temperature then the surface cooled by latent heat of evaporation so the gaseous phases nucleate and cause explosive sublimation.

Raman scattering showed peaks for the as grown and annealing LSM thin films in Fig. 6.

LSM thin film yields four active phonon modes $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ and La (Sr) O_2 extending modes have stretched along c-axis with A_g symmetry. O_2 and La(Sr) vibrations with shifting along a and b axis with E_g symmetry. The weak Raman shift in the wave number range 120.25 to 257.43 cm^{-1} corresponding to A_{1g} phonon signal as reported in Ref. [15].

The bands 301, 303 and 520 cm^{-1} corresponding to silicon Si (100) as mentioned in Refs. [16, 17].

The bands in range $329.06\text{--}459.81\text{ cm}^{-1}$ vibration of MnO_6 octahedral it corresponds to the bond angle changes of $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ with higher frequency than reported by Ref. [15].

The bands $492.06\text{--}596.12\text{ cm}^{-1}$ corresponding to Jahn Teller distortion of MnO_6 with A_g symmetry.

620.06 cm^{-1} band corresponds to the orthogonal cubic phase which is MnO_6 octahedral stretching with symmetric and antisymmetric vibration characteristic peaks.

The bands in range $645.11\text{--}664.50\text{ cm}^{-1}$ corresponding to B_{2g} (breathing mode) with higher frequency than reported by Ref. [18].

All Raman peaks appeared at annealing temperature $1,000\text{ }^\circ\text{C}$ with high crystalline film.

4. Conclusions

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ nanocomposite of proper stoichiometry was successfully synthesized using sol gel method with Rhombohedral crystal system as confirmed by XRD and particles attached with each other as in HR-TEM. LSM thin films were obtained by the PLD method on Si (100) single crystal substrate at different annealing temperatures. The as grown and annealed LSM film at $400\text{ }^\circ\text{C}$ were in amorphous nature and no other peaks detected in XRD. The crystalline LSM film started at annealing temperature $600\text{ }^\circ\text{C}$ and become better with increasing annealing temperature. The average roughness and root mean square roughness found to be decreased for the as grown LSM film and film annealed at temperature 400 and $600\text{ }^\circ\text{C}$ then increased for the films annealed at temperatures of 800 and $1,000\text{ }^\circ\text{C}$ seen by AFM. The bigger particulates in FESEM images due to higher temperatures and weakly bonded particles from target and a crack in film annealed at temperature $1,000\text{ }^\circ\text{C}$. LSM thin films all displays Raman bands and all major peaks revealed at annealing temperature $1,000\text{ }^\circ\text{C}$.

References

- [1] Moriche, R., Marrero-López, D. and Gotor, F. J. 2014. "Chemical and Electrical Properties of LSM Cathodes Prepared by Mechano-synthesis." *Journal of Power Sources* 252: 43-50.
- [2] Tarragó, D. P., Malfatti, C. F. and Sousa, V. C. 2015. "Influence of Fuel on Morphology of LSM Powders Obtained by Solution Combustion Synthesis." *Powder Tech.* 269: 481-7.
- [3] Behera, B. C., Pdhan, P. and Prellier, W. 2015. "Influence of Substrate in All-Ferromagnetic Superlattices." *J. of Magnetism and Magn. Mat.* 388: 22-7.
- [4] Cesário, M. R., Macedo, D. A., Oliveirab, R. M., Pimentel, P. M., Moreira, R. L. and Melo, D. M. 2011. "The Synthesis, Thermal Stability, Crystal Structure and Spectroscopic Study of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ Powder Obtained by the Modified Pechini's Method." *J. of Cer. Proc. Res.* 12: 102-5.
- [5] Hafez, M. A. and Elsayed, H. E. 2006. "Femtosecond Pulsed Laser Deposition of Indium on Si(100)." *J Laser Micro./Nanoengin.* 1 (1): 44-47.
- [6] Miller, J. C. and Haglund, R. F. 1988. *Laser Ablation and Desorption*. Academic Press, London.
- [7] Herklotz, A., Dörr, K., Ward, T. Z., Eres, G., Christen, H. M. and Biegalski, M. 2015 "Stoichiometry Control of Complex Oxides by Sequential Pulsed-Laser Deposition from Binary-Oxide Targets." *Appl. Phys. Lett.* 106: 131601.
- [8] Huber, A.-K., Falk, M., Rohnke, M., Luerssen, B., Amati, M. and Gregoratti, L. et al. 2012. "In Situ Study of Activation and De-Activation of LSM Fuel Cell Cathodes Electrochemistry and Surface Analysis of Thin-Film Electrodes." *J Cat.* 294: 79-88.
- [9] Goktas, A., Aslan, F. and Mutluy, I. H. 2012. "Annealing Effect on the Characteristics of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ Polycrystalline Thin Films Produced by the Sol-Gel Dip Coating Process." *J Mater. Sci. Mat. Electron* 23: 605-11.
- [10] Zhang, D., Yang, L., Liu, Z., Blinn, K., Lee, J.-W. and Liu, M. 2012. "Growth and Characterization of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ Thin Films for Fuel Cell Applications." *App. Surf. Sci.* 258: 6199-203.
- [11] Daengsakul, S., Mongkolkachit, C., Thomas, C., Thomas, I., SIRI, S. and Amornkitpamrung, V. et al. 2009. "Synthesis and Characterization of $\text{LaMnO}_{3+\delta}$ Nanoparticles Prepared by a Simple Thermal Hydro-Decomposition Method." *Optoelectronics and Advanced Materials Rapid Communications* 3 (2): 106-9.
- [12] Xie, H., Huang, H., Cao, N., Zhou, C., Niu, D. and Gao, Y. 2015. "Effects of Annealing on Structure and Composition of LSMO Thin Films." *Phys. B. Cond. Mat.* 477: 14-9.

- [13] Navasery, M, Halim, S. A., Soltani, N., Bahmanrokh, G., Erfani, M. and Chen, S. K. *et al.* 2014, "Growth and Characterization of $\text{La}_{5/8}\text{Sr}_{3/8}\text{MnO}_3$ Thin Films Prepared by Pulsed Laser Deposition on different Substrates." *J Mater Sci: Mater Elect.* 25: 1317-24.
- [14] Tikhii, A. A., Gritskih, V. A., Kara-Murza, S. V. and Korchikova, N. V. 2014. "Optical and Magnetoresistive Properties of Polycrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Films on Crystalline Al_2O_3 and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ Substrates." *Low Temp. Phy.* 40: 968-74.
- [15] Ren, R., Ren, Y., Li, X. and Lei, B., 2016. "Carrier Transport Spin-Orbit Dynamics in Surface Enhanced Raman Shift of Perovskite Films." *Journal of Alloys and Compounds* 662: 290-5.
- [16] Zhang, D., Yang, L., Liu, Z., Blinn, K., Lee, J.-W. and Liu, M. 2012. "Growth and Characterization of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ Thin Films for Fuel Cell Applications." *Appl. Surf. Sci.* 258: 6199-203.
- [17] Khanduri, H., Chandra, M., Vasala, S., Leinberg, S., Lohmus, R. and Ashworth, T. V. *et al.* 2013. "Magnetic and Structural Studies of LaMnO_3 Thin Films Prepared by Atomic Layer Deposition." *J. Phy. D. Appl. Phy.* 46: 175003.
- [18] Fan, J., Xu, L., Zhang, X., Shi, Y., Zhang, W. and Zhu, Y. *et al.* 2015. "Effect of A-Site Average Radius and Cation Disorder on Magnetism and Electronic Properties in Manganite $\text{La}_{0.6}\text{A}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$ (A = Sm, Dy, Er)." *J. Mater. Sci.* 50: 2130-7.