Characterization and Dielectric Properties of $LaMnO_3$ Thin Films by Spin Coating Method

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Abstract - This paper presents $LaMnO_3$ nanostructured thin films were deposited on silicon substrate by using Single Wafer Spin Processor. $LaMnO_3$ powder was firstly prepared by pyrolysis method. The structural, morphology and thermal properties of LMO powder was examined by XRD, SEM and TG-DTA. The films obtained from spin coating technique have been annealed at 500 ºC and 600 ºC for 1 h. Morphology, and structural properties of fabricated $LaMnO_3$ thin films were investigated by SEM and XRD analysis. The objective of this research is to explore the structure, dielectric properties and processing of thin films that contain nanoscale embedded hard particles.

Key words: $LaMnO_3$ power, $LaMnO_3$ thin films, XRD, SEM, Spin Coating machining

I. INTRODUCTION

Nanotechnology is the engineering of systems and materials at the molecular scale. As far as nanomaterials are concerned, $LaMnO_3$ thin film is one of the candidates which has been attracting due to its numerous interesting properties. The actual interest of $LaMnO_3$ nanomaterial in chemistry and solid state physics is due to its excellence in electrical and optical properties.[1] Perovskite $LaMnO_3$ (LMO) has recently attracted renewed attention as a building block of multilayered heterostructures. In its bulk phase, LMO is on A-type antiferromagnetic (AFM) insulator and hole doping by substituting Sr or Ca or La brings it into a ferromagnetic (FM) semiconducting phase. To properly address the physics of LMO-based heterostructures, the physical properties of the LMO layer must be primarily understood. [2]

It is known that LMO easily adopts excess oxygen from its stoichiometric phase. Since the perovskite phase does not allow interstitial oxygen, it has cation vacancies instead. Indeed, there have been several reports of LMO films exhibiting FM and semiconducting behavior where cations vacancies have been proposed as the main cause. Although such non-stoichiometric LMO films might give misleading information when studying the intrinsic properties of the heterostructures, systematic efforts to retrieve and investigate the bulk-like phase in as – grown LMO thin films have not been sufficiently pursued. The possible applications of the LMO thin films are particularly in photo-conductor, UV optoelectronic, integrated sensor and transparent conducting oxide electrode in many important devices. $LaMnO_3$ thin films has received considerable out in a good deal of applications. [3]

Therefore the attention will be given to review the parameters that influence. The structural, optical and electrical properties of LMO thin films prepared by spin coating Technique. Spin coating has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of fluid resin onto the center of a substrate and then spinning the substrate at high speed. Centripetal acceleration will cause the resin to spread to, and eventually off, the edge of the substrate leaving a thin film of resin on the surface. Final film thickness and other properties depend on the nature of the resin (Viscosity, dying rate, percent solids, surface tension etc.) and the parameters chosen for the spin process.[4,5] In this paper, The characterization and dielectric properties of $LaMnO_3$ thin films are successfully deposited on p-Si substrates by sol-based spin-coating technique.

II. EXPERIMENTAL PROCEDURE

The experimental procedure of lanthanum Manganite (LMO) thin films was depicted in a flow chart as figure 1. The raw materials of Lanthanum Chloride and Manganese Chloride were chosen as starting materials. All chemicals were analytical grade and directly used as received without further modification. Distilled water was used as solvent. Firstly, $LaCl_3.7H_2O$ and $MnCl_2.4H_2O$ solutions were mixed together and stirring with magnetic stirrer for six hours at room temperature. During stirring, ammonium carbonate $(NH_4)_3CO_3$ was poured drop by drop in the mixture solution until to get homogeneous and appropriate solution. The precipitates were collected by filtration to obtain the cream of lanthanum maganite composite mixture. Thus LMO powder was obtained when calcinations temperature was 1000 ºC for 30 minutes. Possible formation mechanism of LMO powder was characterized by XRF, XRD, SEM. Thermal analysis of LMO powder was studied by TG-DTA. LMO nanocrystalline materials were fabricated by calcinations of these composite and some new results were achieved.

The substrate used in this study was p-Si (100). The p-Si (100) wafer of dimension (1 cm x 1 cm) and thickness of

280~300 μm were used as substrate. Before film fabrication p-Si (100) substrate was cleaned by using ultrasonic cleaning method. Cleaned Si substrate was heated at 1200ºC to form the Si/SiO_2 substrate. The resulting LMO powder was dissolved by using ethylene glycol and 2-Methoxyethanol. The mixed solution was stirred with magnetic stirrer for the three hours and as in figure 2. After that, the precursor solutions which were then coated on silicon substrate by using Single Wafer Spin Processor (MODEL WS- 400BZ-6NPP/ LITE) as shown in figure 3. The operation parameters were shown in Table 1. The well dissolved precursor solutions were poured onto the cleaned p-Si (100) substrate which was placed on substrate holder of spinner. The spin speed was 1000 rpm, the substrate temperature was 120 ºC and the spinning time was 45 second. After fabrication, LMO thin films were annealed at the temperature 500 ºC and 600 ºC respectively for 1h. Finally, LMO nanoscale thin film was successfully obtained. Phase formation, and structural properties, surface morphology and size of the thin films were investigated with X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

Table (1)
Operation parameters of LMO thin films

Sample	$LnMnO_3$
Substrate	p-Si (100)
Solvent	ethylene glycol and 2-Methoxyethanol
Spin speed	1000 rpm
Spin time	45 s
N_2 gas pressure	60 psi
Vacuum	25.5(inches of Hg)

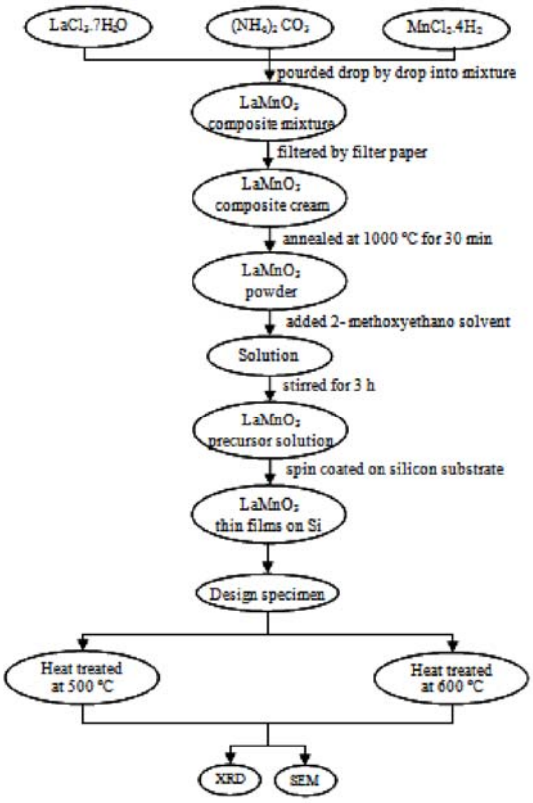

Figure 1 Flow chat for preparation of $LnMnO_3$ thin films

Figure 2 Magnetic stirrer with mixed solution

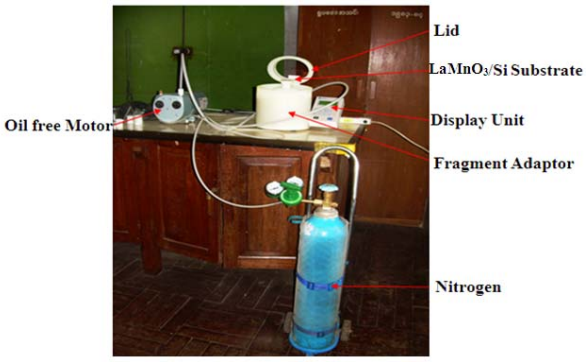

Figure 3 The photograph of spin coating system of the spin processor (MODEL WS-400BZ- 6N PP/LITE)

III. RESULTS AND DISCUSSION

XRD Analysis of LMO Powder and Thin Films

The as-prepared $LaMnO_3$ samples were examined by powder X-ray diffraction (XRD: RIGAKU-RINT 2000 X-ray Diffractometer). XRD is a non – destructive technique for the qualitative and quantitative analysis of the crystalline materials, in the form of powders and films. The information about the crystallographic properties such as crystallite size and lattice parameters over all the samples have been obtained from the XRD profiles. The XRD spectra of $LaMnO_3$ powder was shown in figure (4). Structural characteristics of $LaMnO_3$ film formed on highly polished and defect-free silicon substrate at room temperature 500°C and 600°C were shown in figure (5) (a) and (b). Each refracted rays was recorded as a peak. The peak high was roughly proportional to the ray intensity. The diffraction patterns of specimens were identified by using JCPDS data library. The strongest peak was formed at (202) plane with 20 from 10° of 70°. From XRD measurement, it was formed that the orthorhombic phase of LMO powder was obtained at this temperature range 800°C to 1200°C there were six reflections on XRD profile and all reflection were consistent with that $LaMnO_3$. Standard (JCPDS data library). As shown in figure 5 (a and b), sixth

peaks were formed on the patterns which were well-matched with the typical. LMO and remaining peaks were co-existing peaks caused around 25°. This fact might be probably due to the formation of interface layer between film and Substrate. The maximum intensity was produced at (311) reflection. Some information about the XRD pattern of Powder and films were observed and listed in Table 2.

$LaMnO_3$ Sam	Structural properties		
	powder	film at 500°C	Film at 600°C
Lattice Parameter a (Å)	4.5484	5.7658	5.7212
Lattice Parameter b (Å)	5.2602	6.9622	7.7187
Lattice Parameter c (Å)	6.9399	7.7309	5.4977
FWHM (degree)	0.201	0.435	0.365
Intensity (counts)	270	250	250
Crystallite-size (nm)	41.385	18	24.19

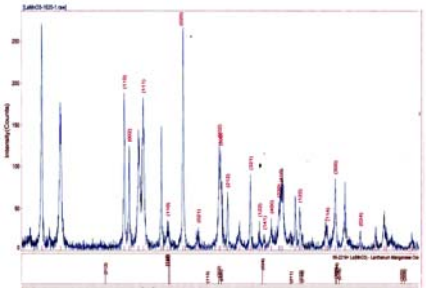

Figure 4 XRD profile of LMO_3 powder at Annealing Temperature 1000°C

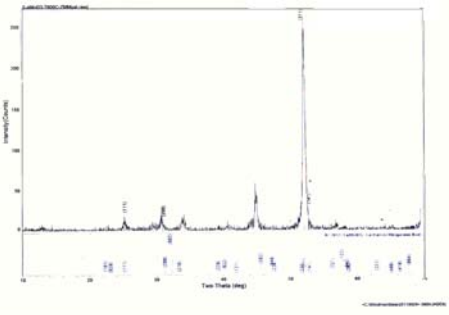

Figure 5 (a) XRD profile of LMO_3 thin film at annealing temperature 500°C

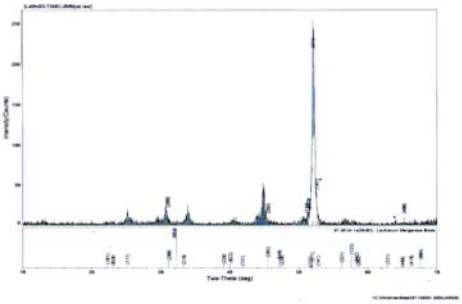

Figure 5 (b) XRD profile of LMO_3 thin film at annealing temperature

Scanning Electron Microscopy Investigation

Surface morphology and micro structural properties of LMO powder and films were carried out by SEM and indicated as figure 6, figure 7 (a and b) According the SEM images, the surface morphology of these films were seemed to be crack – free and uniform grain distribution . The grain orientations were toward right for all films. The grains found to be rounded shaped. The grain distribution on the films at 500°C and 600°C were observed to be dense and smooth. Some pores and grain – growth patterns were also observed on these images. The grain sizes of the LMO films at 500° C and 600°C are to be about 0.54 um and 0.56 um respectively. According these results, it was observed that with the increase in annealing temperature the grain size also increased. SEM analysis indicated that the surface morphology of the grains of LMO film hardly dependent on the process temperature. Film thickness of LMO was measured from cross – sectional SEM micrographs and shown in figure 8 (a and b). The film thickness was found to be 6.5 µm and 3.6 µm for LMO film at room temperature 500° C and 600° C respectively. It was observed that the higher the temperature, the smaller the film of LMO thickness.

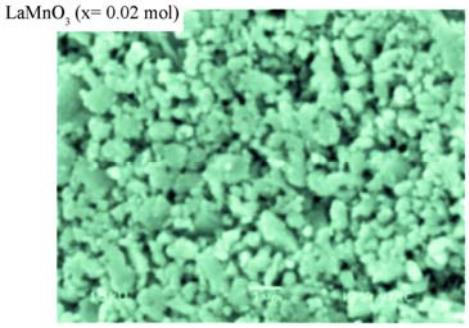

Figure 6 SEM image of $LaMnO_3$ powder at 1000° C

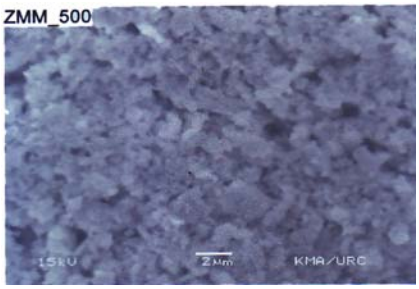

Figure 7 (a) SEM image of $LaMnO_3$ thin film at 500° C

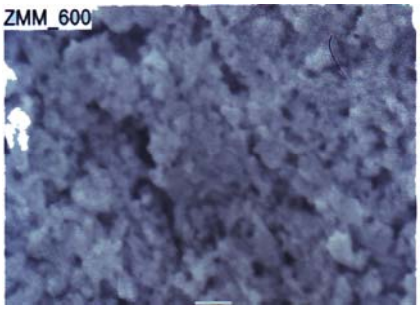

Figure 7 (b) SEM image of $LaMnO_3$ thin film at 600° C

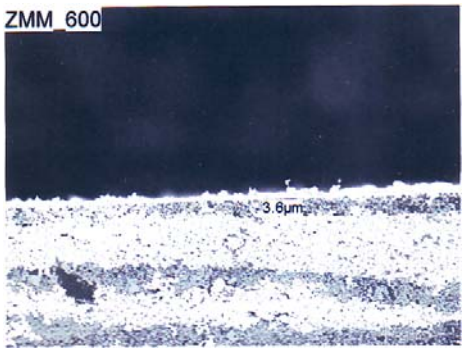

Figure 7 (c) SEM image of $LaMnO_3$ film thickness at 500° C

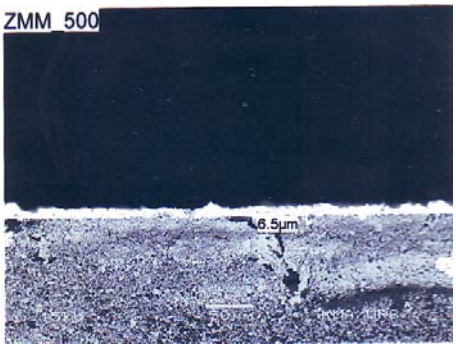

Figure 7 (d) SEM image of $LaMnO_3$ film thickness at 600° C

Dielectric Properties of $LaMnO_3$ thin films

Ferroelectric materials are in general characterized by higher dielectric constants. The higher dielectric constants make these material useful as a capacitor and energy storage devices materials. Dielectric are basically electric insulators which ordinarily do not contain any free charge carriers for conduction. There are the losses of a dielectric at a certain frequency and temperature called "loss-tangent" or dissipation factor tanδ. The dielectric losses associated with the ionic vibrations, the frequencies of which fall in the infrared region are usually referred to as infrared absorption.

The dielectric constant and the loss tangent of LMO films are obtained by measuring the capacitance and dissipation factor with a LCR Digibridge meter (Quad Tech, 1730) operated at 1~ 100kHz, level 1.00V and resistance auto-range. The dielectric and loss factor are increasing with decreasing the frequencies. The dielectric (ε_r) and dissipation factor (tanδ) are seriously depending on frequency, measuring applied alternating voltage level and temperature on the sample. The calculating results of the loss factor, power dissipation and loss current have been reported in table and graph. Variation of conductivity with ω can be studied. The higher frequency from 1 kHz to 100 kHz, the less dielectric and lose factors in versely. The dielectric loss represents average power density loss (P/V) and loss current I_l of the sample for the imaginary parts of the relative permittivity.

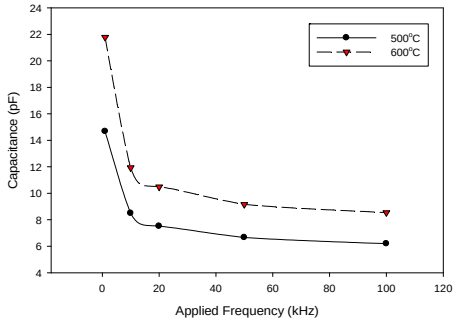

Figure 8 (a) The variation of capacitance with different frequencies

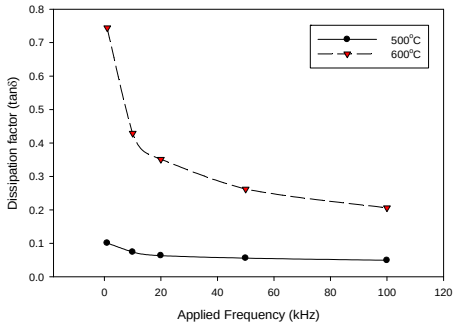

Figure 8 (b) The variation of dissipation factor with different frequencies

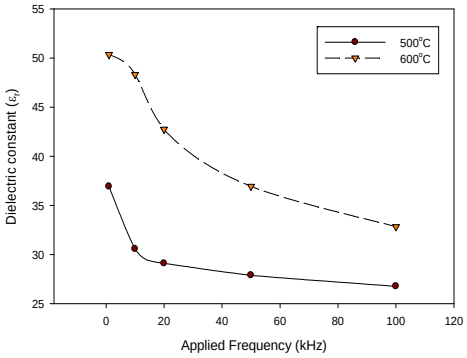

Figure 8(c) The variation of dielectric constant with different frequencies

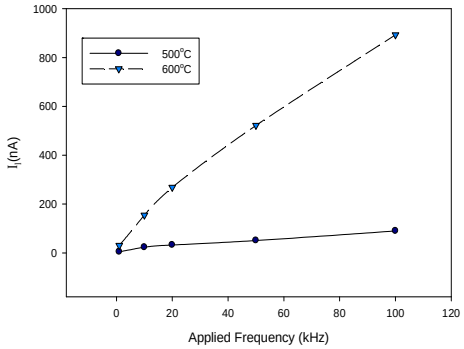

Figure 8 (d) The variation of current loss with different frequencies

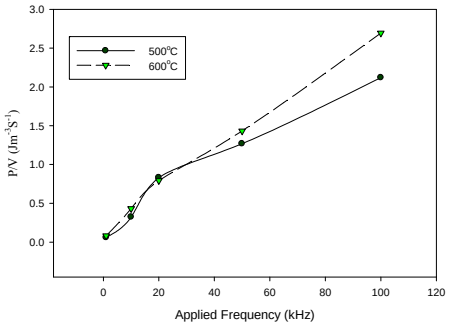

Figure 8 (e) The variation of power dissipation with different frequencies

IV. CONCLUSION

Fabrication of Lanthanum Manganite (LMO) thin films on silicon substrate and its characterization and dielectric properties have been successfully implemented by spin coating Technique. According to XRD analysis, information on lattice parameters, FWHM and crystallite size have been regarded with the as-prepared films and they are listed in Table 2. SEM images were observed that the circular features known as rosette structure with uniform and well – defined grains. It was well known that $LaMnO_3$, thin film provided a good deposition on Si substrate. The effects of the dielectric properties of $LaMnO_3$ films on Si substrate were investigated as shown in figure 8 (a ~ e). The dielectric and dissipation factor are performed at a frequency range from 1kHz to 100 kHz using LCR Digibridge (Quad Tech, 1730). This research observed that when the applied frequency increased, dielectric constant ε_r and dissipation factor tan δ were decreased and loss current I_L was increased. According to the experimental results, the laboratory-grown $LaMnO_3$ thin film was quite well indicated for electrical appliances.

V. ACKNOWLEDGEMENTS

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VI. REFERENCES

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