PULSED LASER DEPOSITION OF $LaFeO_3$ THIN FILMS USING THE TARGET PREPARED BY PECHINI METHOD

Yoshito Tsuchiya[1)], Kento Norota[1)], Yuta Watabe[1)], Takuji Kuroda[1)], Nobuyuki Iwata[1)], Takuya Hashimoto[2)], Hiroshi Yamamoto[1)]

1) College of Science & Technology, Nihon Univ., 7-24-1 Narashinodai, Funabashi-shi, Chiba 274-8501, Japan
2) College of Humanities and Sciences, Nihon Univ., 3-25-40 Sakurajousui, Setagaya-ku, Tokyo 156-8550

Introduction

Compared with the solid state reaction, the Pechini method is known as an excellent process to obtain a compound composed of uniform and quite small particles, and fully reacting. In the pulsed laser deposition (PLD), it is noted that the quality, namely density, of the target determine the film quality. A single crystal target is the best, but it is practically impossible. In Pechini method, the particles with the size of one-tenth in diameter can be calcined. In this study $LaFeO_3$ (LFO) thin films were gown by the PLD method using the highly reacted and dense targets prepared using Pechini method [1,2].

Experimental

The powder of lanthanum oxide La_2O_3 (Furuuchi Science Co., 99.99%), 33.55g, and iron nitrate (III) $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich Co., 99.0%), 83.36g, were weighed to be one to one with the mole ratio of Sr to Fe. The La_2O_3 powder was distributed in the purified water. Nitric acid was dropped in the La_2O_3 dispersed solution until the powder was dissolved. The iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ was also distributed and dissolved in the purified water. The La_2O_3 and $Fe(NO_3)_3 \cdot 9H_2O$ dissolved solution were mixed, and citric acid $C_6H_8O_7$ (Wako and Assay, 98.0%) ,173.15g was added. Continuously ethylene glycol, $C_2H_4(OH)_2$, 93.08ml, (Wako Pure Chemical Industries Ltd., 99.0%) was added. The mole ratio of La : Fe : $C_6H_8O_7$: $C_2H_4(OH)_2$ was 1 : 1 : 2 : 4. Then the mixed solution was heated up to 450°C with the rate of approximately 2.5°C/min. The temperature was maintained at 450ºC until the solution was dehydrated. Igniting the dehydrated gel by blowing, an included organics was evaporated. Thereafter it was ground using agate mortar for one hour. The powder was fired in an alumina crucible at the temperature ranging from 500 to 900ºC for 24 h to remove organics completely.

The powder fired at 800ºC was used for the target to grow LFO thin films. The target was calcined at 1380ºC at the pressure of 300kg/cm^2 in air. The $SrTiO_3$(100) (STO) substrates were ultrasonically cleaned in acetone and ethanol. The cleaned substrate was soaked in pure water for 30 min in ultrasonic bath. The substrate surface was etched by a buffered HF (Daikin Industries, Ltd., pH=5.0) for 45 sec, immediately rinsed by pure water. The etched substrate was annealed at 920 ºC for 6 h in air. The LFO films were deposited by PLD method on the STO(100) substrates using 248 nm KrF excimer laser with the energy density of 2.2 J/cm^2 at the target surface and a repetition rate of 4 Hz. The deposition was carried out for 15 min at 660°C and 20Pa under the atmosphere of 12% ozone with 20 ccm flow rate. The distance between the target and substrate was 53 mm.

Crystalline structure and purity of calcined powder was evaluated with x-ray diffraction (XRD) ($CuK_{\alpha 1}$: 50 kV, 100 mA, RINT-2500, Rigaku Co. Ltd.), and the grain distribution was investigated by a granulometry meter (SALD-3000S, SHIMADZU Co. Ltd.). The LFO thin films were evaluated by scanning probe microscopy (SPM) (dynamic force mode, DFM, Nano Navi, SII Co. Ltd.) and XRD ($CuK_{\alpha 1}$: 40 kV, 30 mA, Rigaku Co. Ltd.).

Results and Discussion

Figure 1 shows the x-ray diffraction (XRD) spectra of powders fired at (a) 500ºC, (b) 600ºC, (c) 700ºC, (d) 800ºC, and (e) 900ºC. The powders were prepared by the Pechini method. At even low temperature of 500ºC, the Bragg diffractions of LFO can be seen without any other phases. Increasing the fired temperatures, the LFO Bragg diffractions were developed probably due to the improvement of LFO crystal caused by the elimination of remained organics. However, peaks of Fe_2O_3 were appeared at 900°C indicated by red arrows. The full width at half maximum (FWHM) of (121) and (240) peaks are summarized in Table 1. Increasing the fired temperature, it was observed that the FWHM of the (121) and (240) plane became smaller.

Table1. FWHM of (121) and (240)

Fired Temperature(°C)	FWHM of (121)	FWHM of (240)
500	0.45	0.57
600	0.35	0.42
700	0.27	0.35
800	0.21	0.29
900	0.20	0.27

Figure 2 shows the fired temperature dependence of grain size with the value of distribution percentage. The inset figure shows grain size distribution of the specimen fired at 800°C, investigated by a granulometry meter. The distribution of the grain size was demonstrated by the appearance of the two peaks, one of which was smaller one, noted by peak 1, and the other one was larger one, noted by peak 2 as is indicated by arrows in the inset figure. The peak center, an allowable error, and intensity of distribution were estimated by a fitting using Gauss function. At 800ºC, the most amounts of powders of the LFO with the smallest particle size was obtained. It is expected that the remained organics were completely eliminated at 800ºC. Therefore the powder fired at 800ºC was used for LFO target.

Figures 3 show the surface images of (a) STO(100) substrate and (b) LFO thin film. The step height of the substrate was approximately 0.37 nm, which is consistent with that of lattice parameter of a STO single crystal. After deposition, particles with the size of approximately 10 nm were dispersed on the substrate terraces. The

step-terraces structure can be still seen. The step height of the film was 0.32 nm.

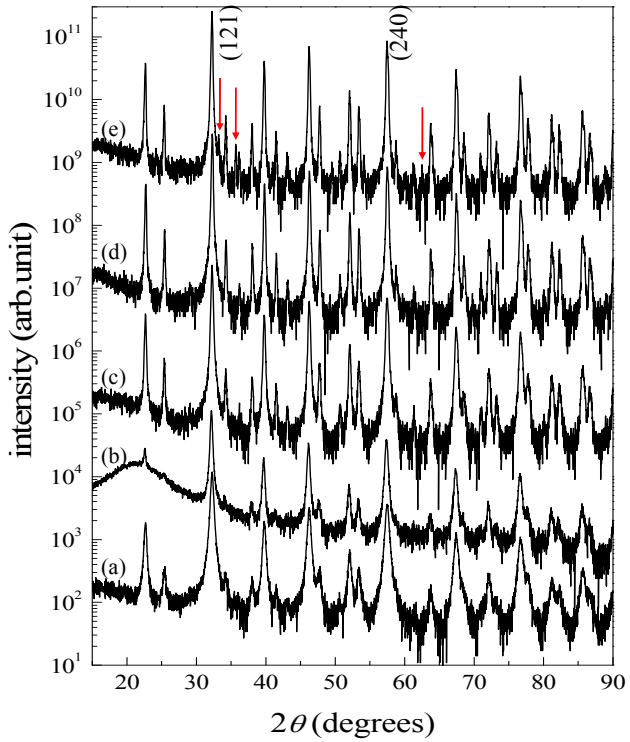

Figure 1 The XRD spectra of the powders fired at (a) 500ºC, (b) 600ºC, (c) 700ºC, (d) 800ºC, and (e) 900ºC. The powders were prepared by Pechini method.

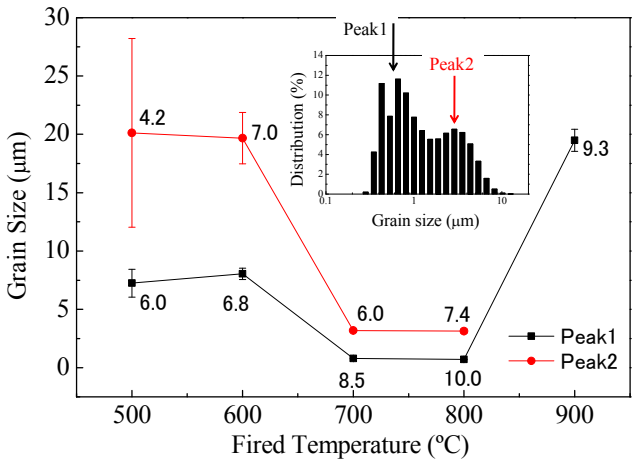

Figure 2 The fired temperature dependence of the grain size. The grain size was distributed from 0.2 to 10 μm as shown in the inset figure, depending on the fired temperature. The position of the peak 1 and 2 denote the center of the smaller and larger grain size.

Figure 5 shows 2θ-θ XRD result of LFO thin film. The Bragg diffractions of the LFO were observed just at the left hand side of the substrate peaks. The inset figure is the magnified picture around LFO(004) Bragg diffraction, which accompany with the Laue oscillation indicated by the dashed arrows. The FWHM of the rocking curve for LFO(004) was 0.052º. The presence of the Laue oscillation and the quite narrow FWHM revealed that the grown LFO film was highly crystalline film.

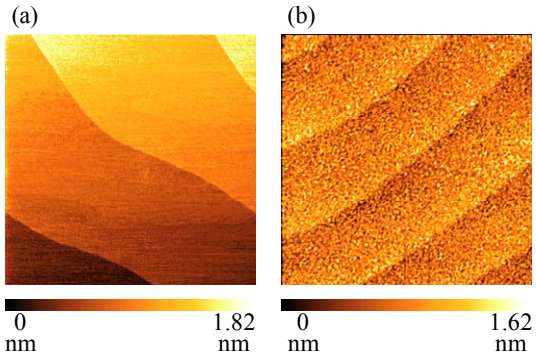

Figure 3 The 2×2μm^2 surface image of (a) surface treated STO(100) substrate and (b) LFO thin film.

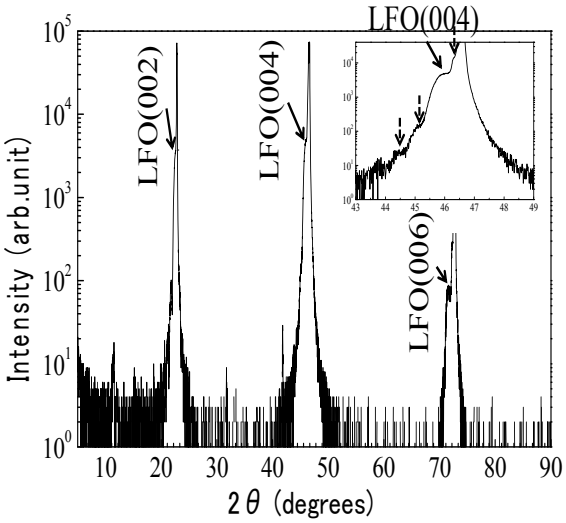

Figure 4 The XRD spectra of the LFO thin film. The peaks indicated by arrows are LFO Bragg diffractions. The inset figure shows the magnified spectrum around LFO(004). The Laue oscillation was observed.

Conclusion

The LFO target was prepared using powder fired at 800ºC by the Pechini method. At 800ºC the smallest powders of the LFO without any other phases were obtained. The LFO film was deposited on STO(100) substrate by PLD method. The surface of the LFO film was covered by a lot of particles with the size of approximately 10 nm in diameter. The XRD results showed the Laue oscillation around the LFO(004) Bragg diffraction and the FWHM of the rocking curve was 0.052º, indicating the film was highly oriented.

References

[1] N.Iwata *et al.*, "Growth of CaFeOx/$LaFeO_3$ Superlattice on $SrTiO_3$(100) Substrate", 2010 Fall Proc. **1292** (2011) K12.16.
[2] M.P.Pechini *et al.*, "METHOD OF PREPARING LEAD AND ALKALINE EARTH TITANATES AND NIOBATES AND COAATING METHOD USING THE SAME TO FORM A CAPACITAOR",Unite States Patent Office,1963

Acknowledgement
This research was supported by KAKENHI (21760013), Nihon Univ. N. research project, and CST Nihon Univ. research project.