Preparation and Properties of Sol-Gel Processed Lead Lanthanum Titanate Thin

Hyun Hoo Kim*
Electronic Department, Doowon Technical College, Kyeonggi-do 456-890, Korea

Jung Geun Lee
Metallurgical Division, Agency for technology and Standards, Kyeonggi-do 427-010, Korea

E-mail : hhkim@doowon.ac.kr

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In order to investigate the dependence of La content in lead lanthanum titanate (PLT) films and heat treatment, sol-gel process has been used. Four types of PLT thin films with the chemical formula, $Pb_{1-X}La_XTi_{1-X/4}O_3$ (x = 18, 21, 24, and 28 mole %) have been fabricated on $Pt/Ti/SiO_2/Si$ multi-layers and ITO/glass substrates. The post-annealing temperature in the range of 400 ~ 700 °C is applied for the formation of perovskite structure in PLT films. The structural, electrical and optical properties of PLT films with the addition of La content are estimated. The film orientation and surface structure of films are studied by XRD (X-ray diffraction) and SEM(scanning electron microscopy). The P-E hysteresis loop become narrower with increasing La content. The average transmittance of the films is about 80 %.

Keywords : PLT, Sol-gel, Annealing temperature, Perovskite, P-E

1. INTRODUCTION

Since ferroelectric ceramic oxides were well known as excellent materials in dielectric, electro-optic, piezoelectric, and pyroelectric properties, they have received increasing attention and also can be used for various device applications, including piezoelectric sensors, nonvolatile memories, pyroelectric detectors, optical wave guides, and optical memories [1]. Compound ceramic oxides of PT family systems are $PbTiO_3$ (PT), $Pb[Zr,Ti]O_3$ (PZT), $[Pb,La]TiO_3$ (PLT), and $[Pb,La][Zr,Ti]O_3$ (PLZT). Particularly, PLT films through a proper control of lanthanum (La) content have a number of properties which make them useful in a variety of applications; for examples, high piezoelectric constant, high dielectric constant, relatively low dissipation factor, high electric resistivity, fairly high pyroelectric coefficient, high optical transmittance, and high electro-optic coefficient [2-3]. The perovskite structure in the ferroelectric phase of $Pb_{1-X}La_XTi_{1-X/4}O_3$ (PLT) oxide assumes one of three structural formations: tetragonal, orthorhomic, or rhombohedral. PLT oxide possesses the perovskite crystal structure described by the general chemical formula ABO_3. The A element (Pb and La) is a large cation situated at the corners of the unit cell, and the B elements (Ti) is a smaller cation located at the body center. The oxygen atoms are positioned at the face centers. Lead titanate ($PbTiO_3$) is a tetragonal ferroelectric perovskite material with the Curie temperature (T_C) of 490 °C, and its tetragonality (c/a ratio) is 1.06 at room temperature. The addition of La to the ferroelectric PT system causes a unit cell contraction. The c/a ratio and T_C decrease monotonically with increasing La content. Therefore, the effect of adding La to the PT oxide is to reduce the stability of the ferroelectric phases in favor of the paraelectric cubic phase.

Several deposition methods have been used to synthesize PLT ceramic thin films, including rf magnetron sputtering, ion beam sputtering, metal-organic decomposition (MOD), metal-organic chemical vapor deposition (MOCVD), excimer laser ablation, and sol-gel solution method, etc [4-8]. Sol-gel processing of various deposition techniques is widely used for the fabrication of ferroelectric oxide thin films with many compositions because of film uniformity in large area, easy control of stoichiometry, relatively low annealing temperature, and simple and inexpensive process.

In this study, PLT thin films with La content of 18 ~ 28 mole % are prepared on $Pt/Ti/SiO_2/Si$ multi-layers and ITO/glass substrates by sol-gel process. The structural, electrical and optical properties of PLT films with change of La content are estimated. The effects of

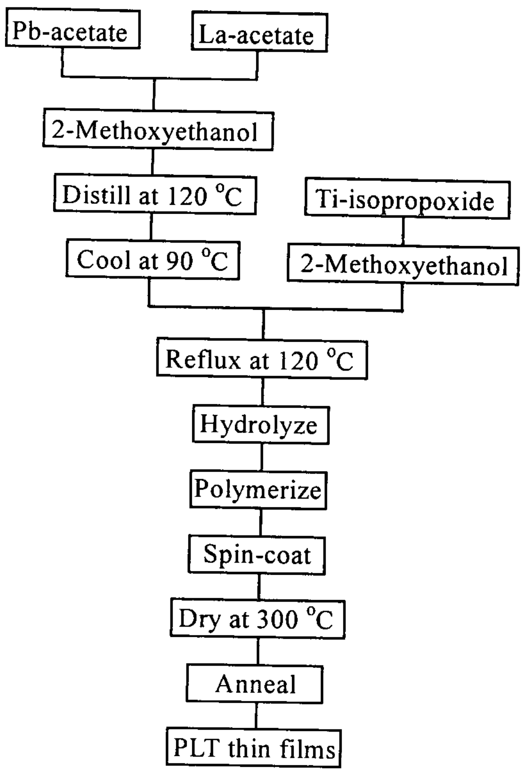


Fig. 1. Flow diagram of PLT precursor solution.

heat treatment in the temperature ranges of 400 ~ 700 °C were investigated on the formation of PLT films.

2. EXPERIMENTAL

A sol-gel process has been used for the fabrication of PLT thin films with the exact chemical formula, $Pb_{1-x}La_xTi_{1-x/4}O_3$ (x = 18 ~ 28 mole %). Lead acetate trihydrate $[Pb(CH_3COO)_2 \cdot 3H_2O]$, lanthanum acetate $[La(CH_3COO)_3 \cdot xH_2O]$, titanium isopropoxide $[Ti(C_3H_7O)_4]$ were used as the raw materials and 2-methoxyethanol ($CH_3OCH_2CH_2OH$) was used as a solvent. Fig. 1 shows the detailed flow diagram for the preparation of precursor solution. Four kinds of films with La content of x = 18, 21, 24 and 28 mole% were adapted and expressed as PLT(18), PLT(21), PLT(24) and PLT(28), respectively. Lead acetate, lanthanum acetate and 2-methoxyethanol were added into a 4-neck flask and distilled under nitrogen flow at 120 °C for 3 hrs. with stirring. The dehydrated solution was cooled to 90 °C, and then titanium isopropoxide with a proper amount of 2-methoxyethanol was added slowly to the solution through a funnel. The solution was refluxed at 120 °C for 3 hrs. The precursor mixture solution was cooled down to room temperature and deposited on $Pt/Ti/SiO_2/Si$ multi layers and ITO/glass substrates by a spin coater at 4000 rpm for 30 sec. Then the films were dried on a hot plate at 300 °C for 10 min. The deposition and drying procedure was repeated several times to obtain a required thickness. Finally, the multi-coated PLT films were heated for post-annealing treatment in the temperature range of 400 ~ 700 °C.

The film thickness measurements were carried out using a surface profilometer (α -step 500, Tensor). In order to investigate the effects of adding La content and annealing temperature in PLT thin films, the crystalline phase and surface microstructure of the films were estimated by XRD using Cu-Kα emission in the range of 20 ~ 70° and SEM, respectively. The thermal decomposition for the dried gels of PLT solution was measured by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The optical transmittance in the visible ranges were performed using a spectrophotometer (UNICAM 8700, Phillips).

3. RESULTS AND DISCUSSION

Fig. 2 shows the thermal analysis data of PLT(24) dried gel under a heating rate of 10 °C/min and argon atmosphere. In the TG curve, weight loss of the gel powder occurs gradually between 200 °C and 500 °C. The broad peak around 150 °C and another peak at 380 °C are due to elimination of water involved in the dried gels and thermal decomposition of the organic compounds, respectively. It is impossible to determine the crystallization temperature of PLT because of the broad exothermic peak from 450 to 600 °C in the DTA trace.

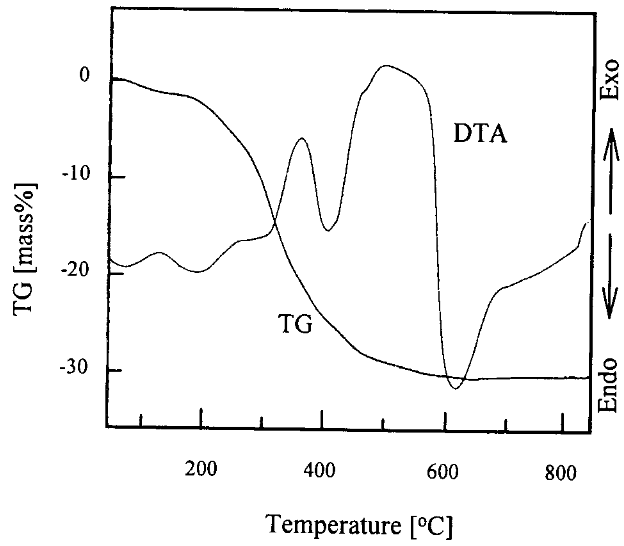


Fig. 2 Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) plots of PLT(24) gel.

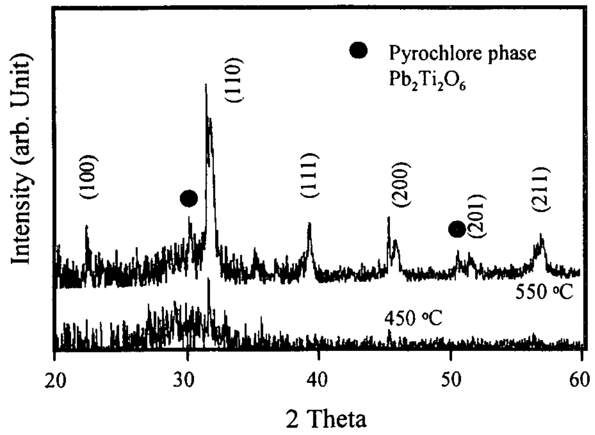


Fig. 3 X-ray diffraction patterns of PLT(21) films deposited on ITO/glass substrate at different annealing temperature.

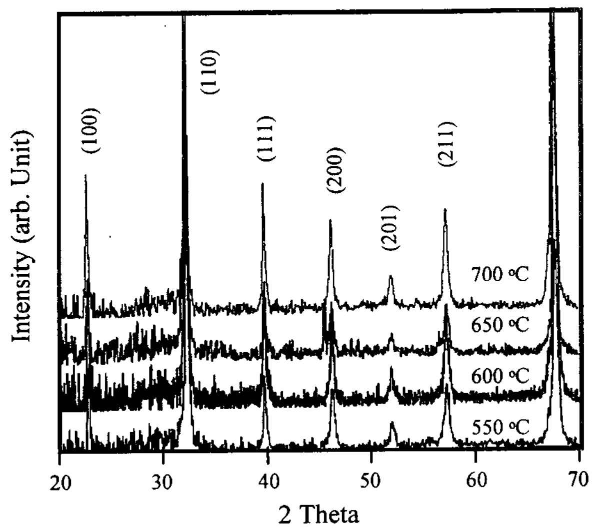
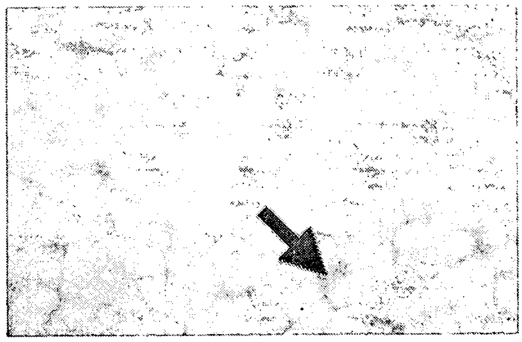
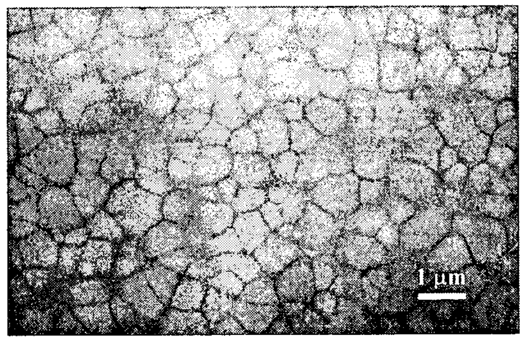


Fig. 4 X-ray diffraction patterns of PLT(28) films deposited on Pt/Ti/SiO2/Si multi layer substrate at different annealing temperature.

Fig. 3 depicts the XRD patterns of the PLT(21) deposited on ITO/glass substrate at different annealing temperature. A broad bump at around of 30° in the PLT films annealed below 450 °C is observed and it means that the PLT films is in the amorphous state. A small amount of pyrochlore $Pb_2Ti_2O_6$ phase seems to appear at 550 °C, as shown in Fig. 3. On the other hand, PLT(21) films annealed at 550 °C are observed several peaks of polycrystalline perovskite phases such as (100), (110), (111), (200), (210) and (211). The XRD patterns of PLT(28) thin films prepared on $Pt/Ti/SiO_2/Si$ substrates at the different annealing temperature from 550 to 700 °C for 5 min are given in Fig. 4. The figure indicates that the duration of 5 min is enough to obtain the perovskite structure at 550 °C and above. As the annealing temperature is increased, each peak which indicates perovskite phase becomes sharper, and the full width at half maximum (FWHM) is likely to decrease and mean better crystallinity. From the above results, the crystalline state of PLT films is found to depend strongly on the annealing condition. The lattice constants are found approximately to be a = b = 0.3957 nm and c = 0.4001 nm for PLT(28) film annealed at 700 °C. It is suggested that the film is crystallized in the tetragonal phase and c/a ratio is 1.011.



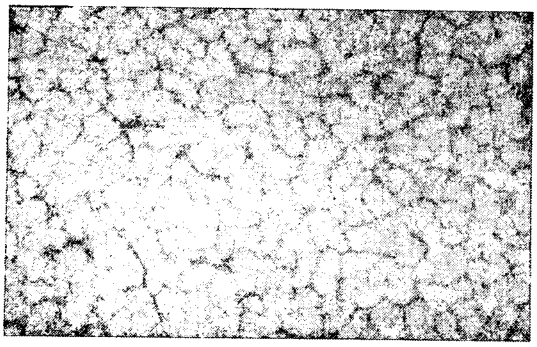
(a) Ta=450 °C



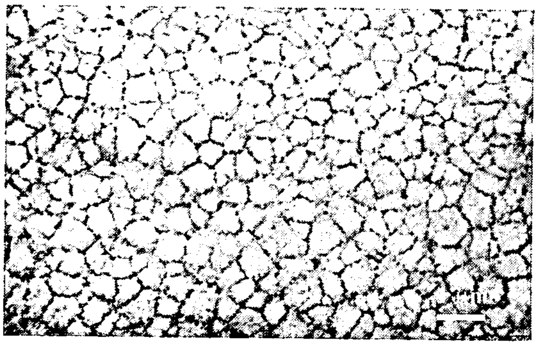
(b) Ta=550 °C

Fig. 5 SEM surface images for PLT(28) on ITO/glass substrate at the annealing temperature of (a) 450 °C and (b) 550 °C.

Fig. 5 shows the SEM surface images for PLT(28) on ITO/glass substrate as a function of the annealing temperature. At the annealing temperature of 450 °C, the film surface exhibits a featureless region that appears amorphous. However, the region seems to develop with a rise in annealing temperature. A cluster structure, which is well defined grains and consists of about 700 nm sized grains, is shown at 550 °C in the Fig. 5(b). The clusters are bounded by dark low density regions marked with an arrow as shown in Fig. 5(a). It seems that the annealing temperature causes thermal etching by PbO evaporation and grain densification which symbolizes the boundaries that could not be observed in the as-deposited PLT films. Fig. 6 shows the SEM surface images for PLT(28) film on $Pt/Ti/SiO_2/Si$ substrate at the



(a) Ta=600 °C

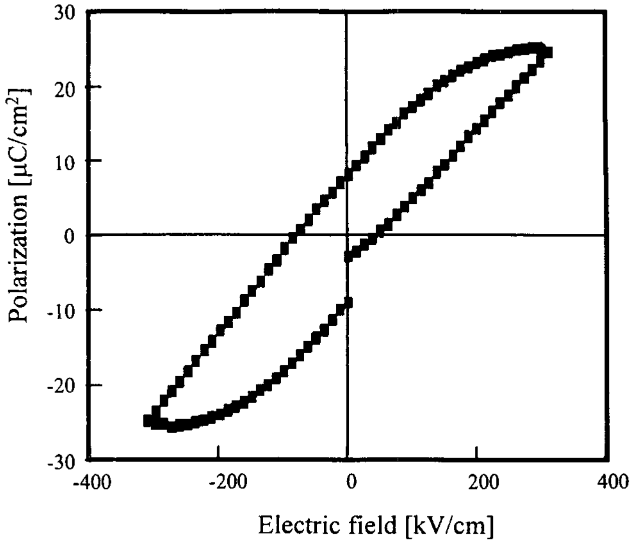


(b) Ta=700 °C

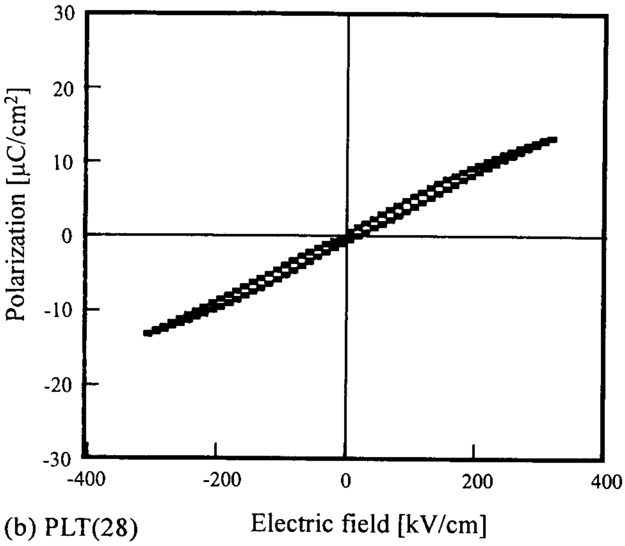
Fig. 6 SEM surface images for PLT(28) film on $Pt/Ti/SiO_2/Si$ substrate at the annealing temperature of (a) 600 and (b) 700 °C.

annealing temperatures of 600 and 700 °C. As the annealing temperature is increased, the formation of clusters and column bundles on the primary grains is more clear. It is noted that the number of pores increases with the increasing temperature. It is considered that the optimum annealing temperature for PLT films is in the range of 550 to 600 °C from SEM data of figure 6 and XRD results of figure 4, since lower temperatures result in incomplete crystallization and higher temperatures cause Pt diffusion in the case of $Pt/Ti/SiO_2/Si$ multi-layer substrate.

Fig. 7 shows the polarization-electric field (P-E) hysteresis loops of PLT(18) and PLT(28) films annealed at 650 °C. As the La content of PLT ceramic compounds is increased from 18 to 28 mole %, the remanent polarization (Pr) decreases from 8.5 $\mu C/cm^2$ to 0.7 $\mu C/cm^2$ and the coercive field (Ec) also declines from 85 kV/cm to 8 kV/cm. The decrease of Ec with increasing La is due to the lowering of the Curie temperature. The P-E curves become narrower with increasing La content and exhibit the phase transformation from ferroelectric perovskite structure to paraelectric cubic ones. It means that the perovskite state of PLT films with the La content of 28 mole % locates near the boundary between ferroelectric and paraelectric phase. However, a slim hysteresis curve of PLT(28) films instead of symmetric



(a) PLT(18)



(b) PLT(28)

Fig. 7 Polarization-electric field (P-E) hysteresis loops of PLT(18) and PLT(28) films annealed at 650 °C.

straight lines is observed. It is considered that the diffuse phase transition of PLT films is caused by the inhomogeneity in microregions as mentioned by Kang and Yoon [9].

Fig. 8 shows the optical transmittance spectra of PLT(21) films on ITO/glass substrate in the visible wavelength ranges as a function of different annealing temperature. The average transmittance of the films is approximately 80 % and is not great difference at the annealing temperature above 400 °C. However, the transmittance of PLT films heat-treated at below 350 °C is poor. This is probably due to the residual organics in the films which do not burn out completely at low drying temperature during the post-heat treatment. From a result, the residual organics cause some voids and micropores in the PLT films.

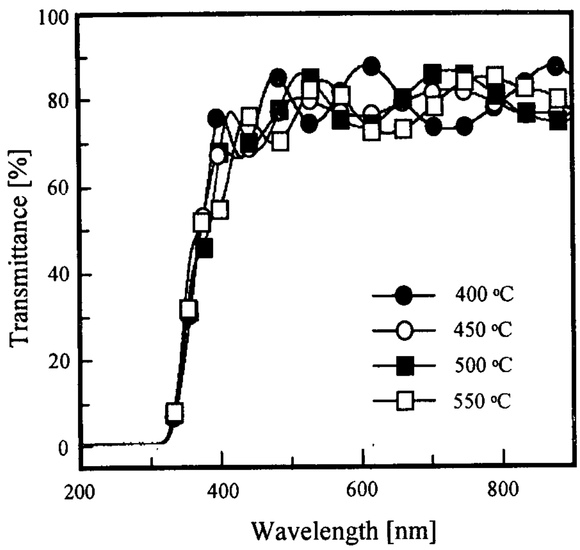


Fig. 8. Optical transmittance spectra of PLT(21) films on ITO/glass substrate as a function of different annealing temperature.

4. CONCLUSIONS

Lead lanthanum titanate (PLT) thin films with the exact chemical formula, $Pb_{1-X}La_XTi_{1-X/4}O_3$ (x = 18, 21, 24, and 28 mole %) are fabricated by sol-gel process. From the thermal analysis data of PLT(24), the weight loss occurs slowly from 200 °C to 500 °C. The crystallization temperature of PLT can not find due to the broad exothermic peak from 450 to 600 °C in the DTA trace. PLT films annealed at 550 °C and above are observed several peaks of perovskite phases from XRD patterns. The crystalline state of PLT films is found to depend strongly on the annealing temperature. The lattice constants are found approximately to be a = b = 0.3957 nm and c = 0.4001 nm for PLT(28) film annealed at 700 °C. As the annealing temperature is increased, the formation of clusters and column bundles on the primary grains is more clear. The number of pores increases with the increasing temperature. Optimum annealing temperature for PLT films appears to be in the range of 550 to 600 °C from SEM image. The P-E curves become narrower with increasing La content, and exhibit the phase transformation from ferroelectric perovskite structure to paraelectric cubic ones. The average transmittance of the films is about 80 %.

REFERENCES

[1] H. Adachi, T. Mitsuya, O. Yamazaki, and K. Wasa, “Ferroelectric PLZT Epitaxial Thin Films on Sapphire Grown by rf Planar Magnetron Sputtering”, *J. Appl. Phys.*, Vol. 60, No. 2, p. 736, 1986.

[2] G. Haertling, *Piezoelectric and Electrooptic Ceramics*, in Ceramic Materials for Electronics edited by R. Buchanan, 2nd Edition, Marcel Dekker, Inc. New York, 1991, p. 129.

[3] J. Carrano, C. Sudhama, V. Chikarmane, J. Lee, A. Tasch, W. Shepherd, and N. Abt, “Electrical and Reliability Properties of PZT Thin Films for ULSI DRAM Application”, *IEEE Ultra. Ferro. Freq. Control*, Vol. 38, No. 6, p. 690, 1991.

[4] M. Okuyama and Y. Hamakawa, “PT Ferroelectric Thin films and Their Pyroelectric Application”, *Ferro.*, Vol. 118, p. 261, 1991.

[5] B. Krupanidhi, H. Hu, and V. Kumar, “Multi-Ion Beam Reactive Sputter Deposition of Ferroelectric PZT Thin Films”, *J. Appl. Phys.*, Vol. 71, p. 376, 1992.

[6] R. Vest, “Metallo-Organic Decomposition Processing of Ferroelectric and Electro-Optic Films: A Review”, *Ferro.*, Vol. 102, p. 53, 1990.

[7] K. Soe, M. Maeda, and L. Suzuki, “Sol-Gel Processing of $Pb_{1-X}La_XTi_{1-X/4}O_3$ Thin Films”, *Jpn. J. Appl. Phys.*, Vol. 35, p. 205, 1996.

[8] D. Roy, S. Krupanidhi and J. Dougherty, “Eximer Laser Ablation of Ferroelectric PZT Thin Films with Low Pressure Direct-Current Glow Discharge”, *J. Vac. Sci. Technol.*, Vol. 10, No. 4A, p. 1827, 1992.

[9] S. Kang and Y. Yoon, “Optical and Electrical Properties of Lanthanum-Modified Lead Titanate Thin Films with Various Lanthanum Concentrations”, *Jpn. J. Appl. Phys.*, Vol. 36, No. 7A, p. 4459, 1997.