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# Preparation of Pb-based Ferroelectric Thin Films by RF-Magnetron Sputtering Method and Their Properties

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**$(PbLa)TiO_3$ (PLT) thin films, a kind of the Pb-based ferroelectrics having a perovskite type crystal structure, were obtained by rf-magnetron sputtering. The PLT thin films were completely oriented to the direction of c-axis. The effect of La concentration on the electrical properties of the thin film were studied. The film containing 15mol% La showed extremely large pyroelectric coefficient of $1.3 \times 10^{-7}C/cm^2K$ and relatively small dielectric constant of 350 (1kHz) at room temperature.**

## 1.INTRODUCTION

Thin films of Pb-based ferroelectrics such as $PbTiO_3$[1,4], $Pb(Zr,Ti)O_3$ (PZT) and $(Pb,La)(Zr,Ti)O_3$ (PLZT) have been studied intensively for applications to dynamic random access memory (DRAM), nonvolatile random access memory, optical device and infrared (IR) sensor, recently.

$Pb_{1-X}La_XTi_{1-X/4}O_3$, prepared by replacing a part of A-site of $PbTiO_3$ by La[2], is expected to exhibit various excellent electrical properties because it is possible to control its Tc by changing the concentration of La[3]. It is reported that the c-axis oriented PLT thin film containing 10mol% La showed good pyroelectric properties[5,6]. The c-axis oriented PLT thin films with La-rich compositions are expected to be excellent pyroelectric materials. However, it is also reported that the preparation of c-axis oriented PLT thin film is difficult in a La-rich region. In this report we describe the preparation of highly c-axis oriented PLT thin films containing more than 15mol% La deposited on Pt/MgO substrates using an rf-magnetron sputtering, and the excellent pyroelectric properties of the films as well as their dielectric and ferroelectric properties.

## 2.EXPERIMENTAL

### 2.1. SAMLE PREPARATION

The composition of the sputtering target powder was $Pb_{1-X}La_XTi_{1-X/4}O_3$, where x=0.15, 0.20, 0.25. These are described as PL15 (x=0.15), PL20 (x=0.20), PL25 ( x=0.25), respectively. Excess PbO powder of 20～30 mol% was added in these materials to compensate the lack of Pb in films. The substrates used were (100)-cleaved and polished MgO single crystals ($12 \times 12 \times 0.5$mm) and (100) oriented platinum thin films (200nm in thickness) as the lower electrode which were deposited on the MgO single crystals by rf-magnetron sputtering at 400～600℃. The PLT thin films of 1～7 $\mu$m thickness were prepared at 500～650℃ by rf-magnetron sputtering. Sputtering conditions are summarized in Table I.

### 2.2. Ferroelectric, dielectric and pyroelectric measurements

A D-E hysteresis loop was observed by the Sawyer-Tower circuit using the sine-wave of 100Hz at room temperature. Dielectric measurements were carried out using an LCR meter (Hewlett Packard, type HP-4284A) in a temperature

Table I. Sputtering Conditions.

| | |
|---|---|
| Substrate temperature | 500~650℃ |
| Input power density | 1.3W/cm² |
| Sputtering gas | $Ar/O_2$,(90/10) |
| Sputtering pressure | 0.5Pa |
| Target | $Pb_{1-X}La_XTi_{(1-X/4)}O_3$ (excess PbO of 20~30mol%) |
| Deposition rate | 4~9nm/min |

range of -100~500℃ at several frequencies between 100Hz and 1MHz. The heating/cooling rates were 5℃/min. Pyroelectric coefficient, $\gamma$ was obtained from the temperature gradient (5 ℃/min) and pyro-electric currents measured by a pA meter (Hewlett Packard, type HP-4140B) in a temperature range of -10~50℃. The measurement was carried out without a poling treatment.

## 3. RESULTS AND DISCUSSION

### 3.1 Crystal Structure

In the previous study we reported that the crystal structures of the PLT thin films were sensitive to the substrate temperature. The films having a perovskite structure were stably obtained between 500~650℃. The orientation of the PLT films were affected by the substrate temperature and the argon to oxygen ratio of sputtering gases.

Figure 1 shows the X-ray diffraction patterns of PLT thin films with different La concentration. The *001* and *002* peaks of the perovskite structure are clearly observed and it is apparent that these films are completely c-axis oriented. It is also observed that the *001* peaks shift to higher angle with increasing of the La concentration. Figure 2 shows the lattice constants of the PLT films as a function of the La concentration. The lattice con-stant of the c-axis is decreasing with increasing of the La concentration, steeply. On the other hand, the lattice constant of the a-axis is

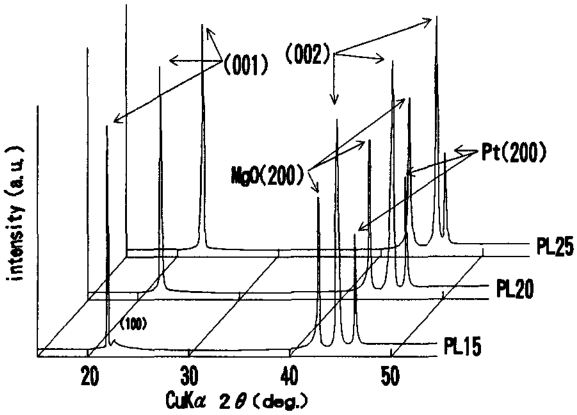


Figure 1. X-ray diffraction patterns of PLT thin films with different La concentration.

increasing with increasing of the La concentration. It is expected that the crystal system of the PLT thin films transform to cubic from tetragonal at the La concentration of x=0.27 of the target composition.

Figure 3 shows the reflection high-energy electron diffraction (RHEED) pattern of the PL15 film on the Pt(100)/MgO(100) substrate. The streak pattern indicating the smooth surface of the PLT thin film are clearly observed. The RHEED patterns indicate that the PLT films were epitaxially grown

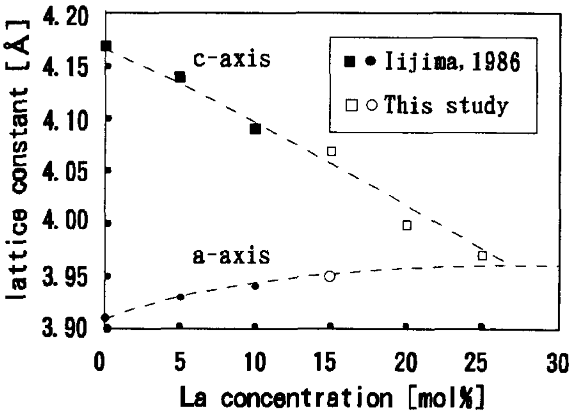


Figure 2. Lattice constants of the PLT films as a function of the La concentration.

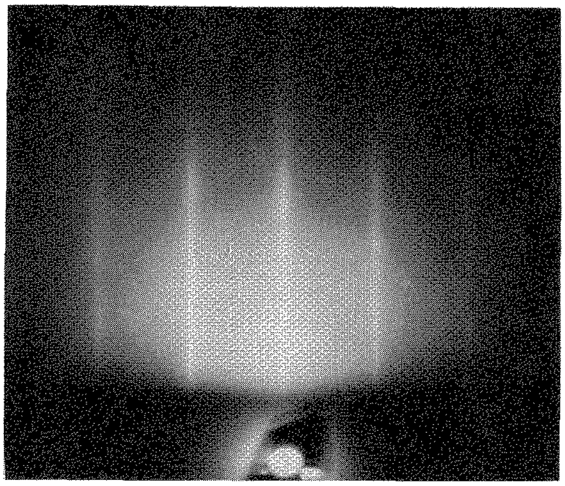

Figure 3. RHEED pattern of the PL15 film on the Pt(100)/MgO(100) substrate.

on the substrate and epitaxial relations are as follows:

(001) PLT // (100) Pt and (100) MgO
<100> PLT // <001> Pt and <001> MgO.

### 3.2. Electric Properties

Figure 4 shows the D–E hysteresis loop of the PL20 (2.84 $\mu$ m in thickness). The remanent polarization Pr and coercive field Ec were 22.4 $\mu$ C/ $cm^2$ and 22.6kV/cm, respectively. The Ec is about half of that expected from the previous study[6]. The decrease of the Ec of the film is due to the lowering of the Tc of the film.

Figure 5 shows the temperature dependence of the relative dielectric constant $\varepsilon_r$ of the PLT thin films of the different La concentration at 1kHz and the inset shows the Curie–Weiss plot of the PL15 above the Tc. The Tc of the PLT thin films shifted to lower temperature with increasing of the La concentration of the films as we would expect from the relationship between the lattice constants and the La concentration. However these value of Tc were about 100℃ higher than that of PLT ceramics[3]. Rossetti et al. reported that the compressive stress developed in the c–axis oriented $PbTiO_3$

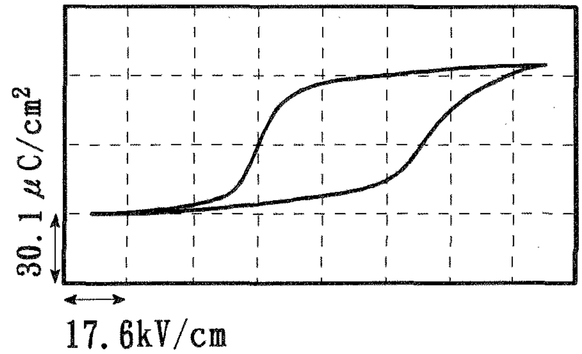


Figure 4. the D–E hysteresis loop of the PL20 film (2.84 $\mu$ m in thickness).

thin film led to a sub–stantial shift in the Tc[7]. TEM observation revealed that lattice mismatch between substrate and film was accommodated by the misfit dislocations at the interface between PLT and substrate and the difference of the expansion coefficient between the PLT film and MgO substrate directly contribute to the compressive stress[8]. In this point of view, it is conceived that the shift of Tc is attributed to the compressive stress from the

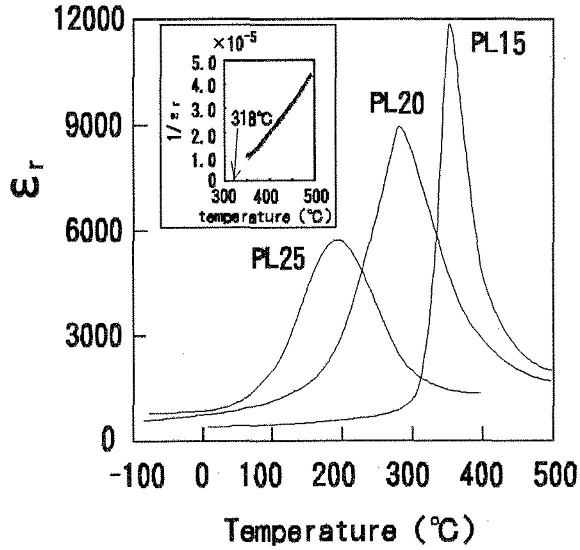


Figure 5. The temperature dependence of the relative dielectric constant $\varepsilon_r$ of the PLT thin films at 1kHz and the inset shows the Curie–Weiss plot of the PL15 above the Tc.

Table II. Pyroelectric properties of PLT thin films

| | $\varepsilon r$ | $\gamma$ ($\times 10^{-7}$C/cm$^2$℃) | Fv($\times 10^{-10}$Ccm/J) | Cv($\times$J/cm$^3$℃) | Tc(℃) |
|---|---|---|---|---|---|
| $PbTiO_3$(ceramics) | 190 | 0.2 | 0.3 | 3.2 | 490 |
| PL10(La 10mol%) | 200-240 | 0.4-0.6 | 0.5-1.0 | 3.2 | 330 |
| PL15(La 15mol%) | 350 | 1.3 | 1.2 | 3.2 | 350 |
| PL20(La 20mol%) | 630 | 0.7 | 0.4 | 3.2 | 280 |

MgO substrate.

The $\varepsilon_r$ achieved a maximum, $\varepsilon_{max}$, at Tc. It is noticeable that the values of $\varepsilon_{max}$ were comparable to those of PLT bulk ceramics[3]. The $\varepsilon_{max}$ were decreasing with the increasing of the La concentration and a broadening of the dielectric phase transition of the film was observed, as compared with bulk materials. The Curie constant of PL15 film was 4.12$\times 10^5$℃ and Curie-Weiss temperature was 318℃. The Curie constant of the films is comparable with that of the bulk ceramics. It seems that the PLT thin film exhibits the first order phase transition because the Curie-Weiss temperature was lower than Tc about 32℃.

Table 2 shows the pyroelectric properties of the PLT thin films. The $\gamma$ of PL15 was very large and it was 3～4 times larger than that of PL10. Figure of merit, Fv (= $\gamma$ /( $\varepsilon_r$• Cv): where Cv is volume specific heat, for IR sensor of this material is 4 times lager than that of $PbTiO_3$ and 1.7 times lager than that of PLT (X=0.10) thin film.

## 4. CONCLUSION

Highly c-axis oriented PLT thin films containing more than 15mol% La were obtained by rf-magnetron sputtering. The PL15 (X=0.15) thin films possessing of excellent pyroelectric properties were obtained by controlling sputtering conditions, precisely. Particularly, proper supply of Pb on growing surface make it possible to prepare the PLT thin films having satisfactory crystallinity and large $\alpha$. RHEED and TEM observations confirmed that c-axis oriented PLT thin films were epitaxially grown on the (100)Pt/MgO substrate with the epitaxial relation of (100)Pt//(001)PLT and <100>Pt//<001>PLT. The epitaxial temperature in this direction was about 600℃. In result, excellent pyroelectric properties of the PLT thin film was achieved: $\gamma$ =1.3$\times 10^{-7}$C/cm$^2$K, $\varepsilon_r$=350, Fv=1.2 $\times 10^{-10}$Ccm/J. Fv of this film is 4 and 1.7 times lager than those of $PbTiO_3$ ceramics and PL10 thin film, respectively. The temperature dependences of dielectric constant showed decreasing of Tc and broadening of dielectric phase transition with increasing of La concentration.

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