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Pyroelectric Characteristics of La-modified $PbTiO_3$ Thin Films Prepared by Multi-Ion-Beam Sputtering

I. Kanno[a], R. Takayama[a], and T. Hirao[b]

[a]Human Environment Research Laboratory, Matsushita Electric Industrial Co., Ltd., 3-4 Hikaridai, Seika-cho, Kyoto 619-02, Japan

[b]Matsushita Technoresearch, Inc., 3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570, Japan

Very thin La-modified $PbTiO_3$ (PLT) films less than 200 nm in thickness have been investigated from the viewpoint of pyroelectricity. Highly c-axis oriented PLT films could be epitaxially grown on (100)Pt-coated MgO substrates using a multi-ion-beam sputtering technique. Sufficient dielectric and pyroelectric properties could be obtained for as-deposited PLT films as thin as 100 nm. The PLT film with La concentration of 18 mol% shows excellent pyroelectric coefficient γ as high as 5.5×10^{-8} C/cm^2K. The relative dielectric constant ε_r of the PLT films remarkably varied with the La concentration from 67 (La = 0 mol%) to 715 (La = 21 mol%).

1. INTRODUCTION

Pyroelectric infrared sensors have various advantages of a room temperature operation and a wavelength independent responsibility. Recently considerable attention has been focused on the Pb-based ferroelectric thin films for the remote sensing system because of their higher sensitivity and responsibility for the infrared detection rather than bulk ceramics. Various techniques have been applied for preparation of pyroelectric thin films such as sol-gel process [1], pulsed laser ablation [2], and especially rf-sputtering [3,4]. It has already reported that the La-modified $PbTiO_3$ (PLT) thin films fabricated by rf-sputtering had the excellent pyroelectric properties with coefficient (γ) and low relative dielectric constant (ε_r) [3]. Furthermore, these films had the polarization directed to the same direction without poling treatment. However, more than 1μm in thickness was necessary to get sufficient pyroelectricity and the properties of PLT films of the thickness less than 1μm have been unclear so far. For further progress of the pyroelectric properties, it is necessary to grow high-quality PLT films and investigate the electric properties of the very thin films about 100 nm in thickness. In this study, we have fabricated very thin PLT thin films less than 200 nm using a multi-ion-beam sputtering technique. This method has various advantages for the preparation of high-quality ferroelectric thin films such as (1) deposition in high vacuum, (2) accurate controllability of the film composition and (3) prevention from plasma damage. Using this technique, we have successfully grown various Pb-based dielectric thin films such as $PbTiO_3$, $Pb(Zr,Ti)O_3$, $PbZrO_3$ and $PbTiO_3/PbZrO_3$ superlattices [5-8]. In this report, we describe the preparation of very thin PLT films and their crystalline and electrical properties.

2. EXPERIMENTAL

The $(Pb_{1-x}La_x)Ti_{1-x/4}O_3$ (PLT) films were deposited using the multi-ion-beam sputtering. The substrates used were (100)Pt-coated (100)MgO single crystals which were heated at 400 °C. For the deposition of the PLT films, Pb, La and Ti metal targets were simultaneously sputtered using individual Ar^+ ion beams which were accelerated at 1100V. Film composition was controlled by Ar^+ ion beam currents. Oxygen gas was introduced near the substrate to oxidize the sputtered species. In order to study the dependence on the film thickness, several PLT films (x=0.08) with the thickness from 50 nm to 200 nm were prepared. In addition the PLT films with various La concentrations ranging from x=0 and 0.37 were also fabricated to investigate the

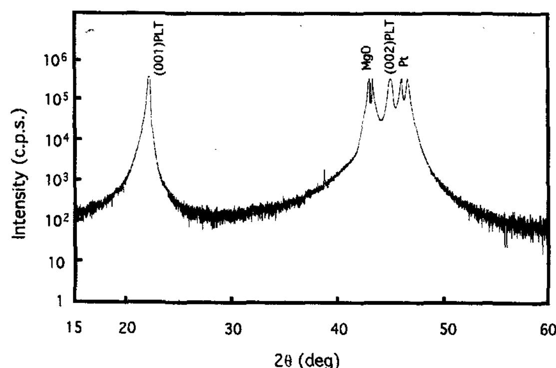

Figure 1. XRD pattern of the PLT films (x=0.1, 100 nm) grown on (100)Pt/MgO substrate.

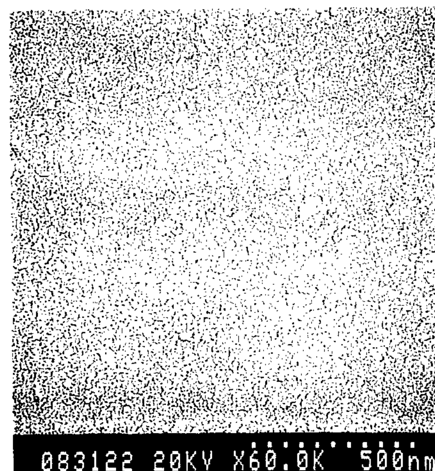

Figure 2. SEM micrograph of the PLT film (x=0.08, 50 nm) deposited on (100)Pt/MgO.

dependence of the electric properties.

The crystalline structure of the prepared PLT films was examined by x-ray diffraction (XRD) measurements using CuKα radiation. The composition of the films was estimated by wavelength dispersive x-ray spectrometer (WDX) to prepare stoichiometric PLT films and determine La concentration. Surface morphology of the prepared films was observed using scanning electron microscope (SEM).

The electric properties of the PLT films were measured with gold top electrodes of 0.3 mm in diameter. The relative dielectric constant ε_r was measured using an impedance analyzer. Furthermore, pyroelectric properties were also examined for as-deposited films without poling treatments. Pyroelctric coefficient γ was determined by the pyroelectric current which was measured by a pA-meter with the temperature gradient between 20 °C and 30 °C.

3. RESULTS AND DISCUSSION

3.1 Film structure

Figure 1 shows the XRD pattern of the as-deposited PLT film (x=0.1, 100 nm). This pattern indicated that the perovskite PLT films were epitaxially grown on the (100)Pt/MgO substrates. Furthermore, this film exhibited highly c-axis orientation without any other orientations. Almost similar XRD patterns with single orientation were also confirmed for the other PLT films with La concentration of x = 0 ~ 0.37 and the film thickness of 50 ~ 200 nm.

Figure 2 shows the surface morphology of the PLT film (x=0.08, 50 nm). This SEM micrograph revealed that the film had very flat and smooth surface and neither grain or domain structures could be observed on the surface. The homogeneous surface structure of the PLT films suggests that the films were grown in two-dimensional layer-by-layer mode on the substrate, which led to high-density PLT films with excellent crystallinity as shown in Fig. 1.

3.2 Thickness dependence

The electric properties of the PLT films with La concentration of x = 0.08 were examined as a function of the film thickness ranging from 50 to 200 nm. Figure 3 shows the relation between relative dielectric constant ε_r and film thickness. The dielectric constant ε_r of any PLT films was about 150 and the degradation of ε_r with decreasing the thickness was hardly observed. These results correspond to the thickness dependence of ε_r for the PZT films prepared by a multi-ion-beam sputtering [6]. These good dielectric properties of the films with the thickness less than 100 nm are attributed to the dense structure of the PLT films as shown in Fig. 2. It also suggests that the layer with degraded crystalline structure does not exist at the interface between films and substrates.

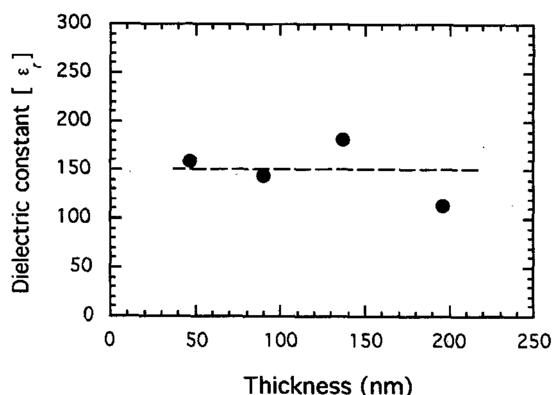

Figure 3. Relative dielectric constant of the PLT (x=0.08) films as a function of the film thickness.

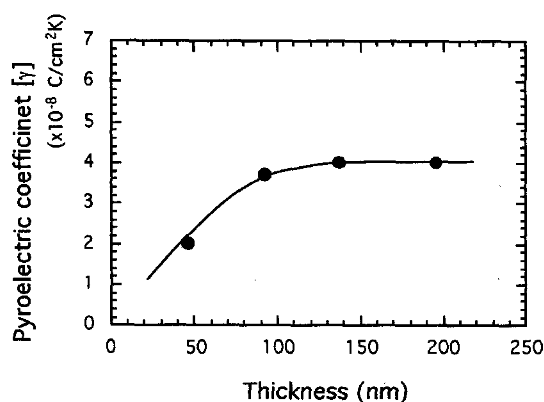

Figure 4. Pyroelectric coefficient of the PLT films (x=0.08) as a function of the film thickness.

On the other hand, Fig. 4 shows the dependence of pyroelectric coefficient γ of as-deposited PLT films on the film thickness. The pyroelectric coefficient γ scarcely decreased until 50 nm in thickness and the sufficient pyroelectric coefficient γ about 4.0×10^{-8} C/cm^2K was obtained for the films (200 ~ 100 nm) without poling treatments. This result indicates that the polarization of the PLT films deposited by a multi-ion-beam sputtering are directed toward upside of the films inherently, which is similar to the PLT films deposited by rf-sputtering [3]. Furthermore, these very thin PLT films posses almost equivalent pyroelectric coefficient γ to the PLT films more than 1 μm in thickness deposited by rf-sputtering, which was reported to have γ as high as 5.3×10^{-8} C/cm^2K. These excellent dielectric and pyroelectric properties of the PLT films prepared by the multi-ion-beam sputtering are attributed to the excellent crystalline structure.

3.3 Dependence on La concentration

The electric properties of the PLT films about 100 nm in thickness were investigated as a function of La concentration of x in $(Pb_{1-x}La_x)Ti_{1-x/4}O_3$ system. Figure 5 shows the relation between relative dielectric constant ε_r of the PLT films with La concentration from x = 0 to x = 0.37. The dielectric constant ε_r of the $PbTiO_3$ film was about 67 and it gradually increases as the La concentration (x) increases. The maximum $\varepsilon_r \sim 715$ was observed for the PLT film with x = 0.21 from which dielectric

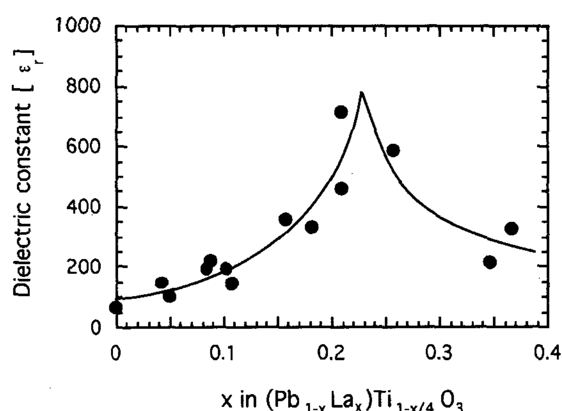

Figure 5. Relative dielectric constant of the PLT films (100 nm) as a function of La concentration.

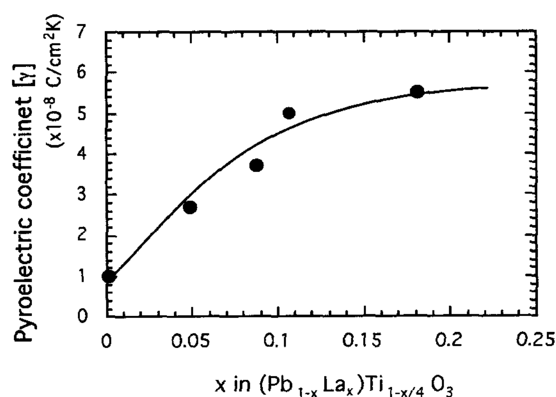

Figure 6. Pyroelectrric coefficnt of the PLT films (100 nm) as a function of La concentration.

constant ε_r decreased as x increases. In the case of the bulk ceramics, it was reported that a maximum ε_r is obtained at x = 0.26 where phase transition from tetragonal to cubic structure occurs [9]. This indicates that the phase transition also occurs for the very thin PLT films as thin as 100 nm at the almost same composition of bulk PLT ceramics.

Pyroelectric coefficient γ was estimated as a function of La concentration x. With increasing La concentration, pyroelectric coefficient γ gradually increased up to 5.5×10^{-8} C/cm^2K at x = 0.18 which correspond to the PLT films prepared by rf-sputtering. In this study, we demonstrated that the very thin PLT films had sufficient dielectric and pyroelectric properties even in the thickness less than 100 nm. It should be due to the high-quality of the PLT thin films with excellent crystalline structure.

4. CONCLUSIONS

Highly c-axis oriented PLT films could be epitaxially grown on (100)Pt-coated MgO substrates using multi-ion-beam sputtering. SEM measurement revealed that the PLT films had very smooth and homogeneous surface.

Electric measurements demonstrated that the as-deposited PLT films exhibited sufficient dielectric and pyroelectric properties even in a very thin thickness less than 100 nm. The PLT films with La concentration of x=0.18 showed the pyroelectric coefficient γ as high as 5.5×10^{-8} C/cm^2K. The relative dielectric constant ε_r of the PLT films reached to 715 at x = 0.21.

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REFERENCES

1. D. L. Polla, Chian-ping Ye, and T. Tamagawa, Appl. Phys. Lett. 59 (1991)3539
2. H. Tabata, T. Kawai, O. Murata and S. Kawai, Appl. Phys. Lett. 56 (1990) 1576
3. K. Iijima, R. Takayama, Y. Tomita, and I. Ueda, J. Appl. Phys 60 (1986) 2914
4. R. Takayama, Y. Tomita, K. Iijima and I. Ueda, J. Appl. Phys. 61 (1987) 411
5. I. Kanno, T. Kamada, S. Hayashi, M. Kitagawa and T. Hirao, Jpn. J. Appl. Phys. 32 (1993) L950
6. I. Kanno, S. Hayashi, T. Kamada, M. Kitagawa and T. Hirao, Jpn. J. Appl. Phys. 32 (1993) 4057
7. I. Kanno, S. Hayashi, M. Kitagawa and T. Hirao, Appl. Phys. Lett. 66 (1995) 145
8. I. Kanno, S. Hayashi, R. Takayama and T. Hirao, Appl. Phys. Lett. 68 (1996) 328
9. G. H. Haertling and C. E. Land, J. Ammer. Ceram. Soc. 54 (1971) 1