Crystallographic Properties of La- and Mg-Modified PbTiO₃ Thin Films Prepared by RF-Magnetron Sputtering Method

Masafumi KOBUNE, Satoshi FUJII, Kenji AKAMATSU, Ryoichi TAKAYAMA* and
Atsushi TOMOZAWA*

Department of Applied Chemistry, Faculty of Engineering, Himeji Institute of Technology, 2167, Shosha, Himeji-shi 671-22

*Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., 3-4, Hikaridai, Seika-cho, Souraku-gun, Kyoto-fu 619-02

高周波マグネトロンスパッタリング法により作製した La 及び Mg 添加の PbTiO₃ 薄膜の結晶学的性質

小舟正文・藤井 知・赤松謙次・高山良一*・友澤 淳*

姫路工業大学工学部応用化学科, 671-22 姫路市書写 2167

*松下電器産業(株)中央研究所, 619-02 京都府相楽郡精華町光台 3-4

[Received August 22, 1994; Accepted November 22, 1994]

Highly *c*-axis-oriented lanthanum- and magnesium-modified PbTiO₃ thin films with compositions of $\{(1-x)\text{Pb}_{0.9}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3 + x\text{MgO}\}$, where $x=0-0.025$ (PLMT), were prepared on (100)-oriented Pt film electrodes/(100)MgO single-crystal substrate by rf-magnetron sputtering method. The *c*-axis orientation, crystallinity, and structure of surface and cross section of films obtained were investigated in detail. From the viewpoint of the crystallographic properties, PLMT films with compositions of $x=0.005-0.010$ show great promise as new element thin-film materials.

Key-words : *Pyroelectric infrared detector, Element material, PbTiO₃, Thin film, Figure of merit, Spontaneous polarization*

1. Introduction

In recent years, PbTiO₃-system films have attracted much attention as excellent ferroelectric,¹⁾ pyroelectric²⁾⁻⁶⁾ and piezoelectric materials.⁷⁾ With respect to the development of a new element thin-film material, the authors have previously reported highly *c*-axis-oriented lanthanum-modified PbTiO₃ thin films with compositions of $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$, where $x=0.05-0.15$ (hereafter "PLT")²⁾⁻⁴⁾ and magnesium-modified PbTiO₃ thin films with compositions of $\text{Pb}(\text{Mg}_x\text{Ti}_{1-x})\text{O}_{3-x}$, where $x=0.015-0.090$ (hereafter "PMT")^{5),6)} by rf-magnetron sputtering method. Both films described above showed excellent crystallinity with good epitaxy on (100)-oriented Pt film electrodes/(100) MgO single-crystal substrates, because they had densely packed microstructure when La was partially substituted at the A-site in the case of the former and a small amount of Mg was successfully substituted at the B-site in PbTiO₃ in the case of the latter. However, the preparation of simultaneous lanthanum- and magnesium-modified PbTiO₃ thin films and their crystallographic properties have not been reported yet.

In this study, by adding a small amount of Mg to

the composition of PLT ($x=0.1$; PL10), we tried to synthesize lanthanum- and magnesium-modified PbTiO₃ thin films with compositions of $\{(1-x)\text{Pb}_{0.9}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3 + x\text{MgO}\}$, where $x=0-0.025$ (hereafter "PLMT"), containing the composition of PL10 by rf-magnetron sputtering method. The degree of *c*-axis orientation, crystallinity, tetragonality and microstructure of the obtained films are investigated. Moreover, on the basis of the crystallographic properties described previously, the optimum range for the amount of Mg addition is clarified in this report.

2. Experimental

PLMT thin films were prepared by rf-magnetron sputtering method. The substrates used in this study were (100)-cleaved, polished and surface-treated MgO single crystals (products of Tateho Chemical Ind., dimensions: $7.0 \times 7.0 \times 0.5 \text{ mm}^3$). The procedure of the surface treatment stated above is as follows: the mirror-polished MgO single crystals were chemically etched in the 4.37 M H₃PO₄ solution in an ultrasonic cleaner for 5 min, and then oxygen-annealed at 1100°C for 10h.⁸⁾ (100)-oriented Pt thin-film electrodes with about 0.1 μm thickness were deposited on the MgO substrates by rf-magnetron sputtering method. The temperatures were measured by a Pt-Pt/Rh 13% thermocouple, which was inserted into the center of the heating block equipped with sheathed heater (maximum temperature in common use: 800°C) as a heating element. The sputtering conditions are the substrate temperature of 600°C, atmosphere of Ar 50% and O₂ 50%, and gas pressure of 0.5 Pa.⁹⁾

The sputtering targets used were mixtures of calcined PLMT powders and PbO powder. The compositions are represented by the formula $[0.8\{(1-x)\text{Pb}_{0.9}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3 + x\text{MgO}\} + 0.2\text{PbO}]$, where $x=0, 0.0025, 0.005, 0.0075, 0.010, 0.015, 0.020$ and 0.025 , and are denoted as follows: PL10, PLM2.5, PLM5,

Table 1. Sputtering Conditions for Preparation of PLMT Thin Films

Input power density	2.0	[W/cm ²]
Sputtering gas	Ar/O ₂ = 90/10	
Gas pressure	0.50	[Pa]
Substrate temperature	917	[K]
Target-substrate distance	64	[mm]
Film thickness	1~2	[μm]
Deposition rate	4.0	[nm/min]
Cooling rate	30	[K/min]

PLM7.5, PLM10, PLM15, PLM20 and PLM25, respectively. Excess PbO powder of 20 mol% was added to these targets to compensate for loss of Pb from the sputtered films.⁹⁾ In addition, the PLMT powders described above were prepared according to the procedure shown below: the starting raw materials were guaranteed reagents of PbO, La₂O₃, MgCO₃ and TiO₂. The components weighed in appropriate proportions were sufficiently mixed in ethanol in an agate mortar. After the mixture was dried at 80°C for 6h, it was calcined in a high-purity magnesia crucible in air at 750°C for 3h. After the calcines were again ground in the same mortar, they were employed as PLMT powders. These powders were filled and pressed at about 250 kg/cm² in shallow Cu dishes of around 0.1 m diameter.

The substrates were fixed on a heating block with a stainless steel (SUS 304) mask of 0.5 mm thickness. The deposition area of PLMT films is 5 mm in diameter. The sputtering conditions for the synthesis of PLMT thin films are summarized in Table 1.

The Mg contents of some of the fabricated films were analyzed by an electron probe microanalyzer (EPMA; JEOL, JXA-8900R) equipped with a wavelength dispersive X-ray spectroscopy (WDS).

The lattice constant, crystalline phase, *c*-axis orientation and crystallinity of PLMT films obtained were analyzed using an X-ray diffractometer (XRD; Rigaku, RINT1500). The lattice constants were determined by applying least squares procedures to the X-ray diffraction method with high-purity silicon powder (NIST-640b) as an external standard, using (002), (003), (200) and (300) reflections of Cu K α radiation. The degree of *c*-axis orientation α for the tetragonal structure is defined by

$$\alpha = I(001) / \{I(001) + I(100)\} \quad (1)$$

where $I(001)$ and $I(100)$ represent the X-ray diffraction intensities of (001) and (100) reflections, respectively. The crystallinity was evaluated in terms of measuring half-width $\Delta\theta$ of X-ray rocking curves of (001) reflection. Furthermore, the microstructure of PLMT films was observed by field-emission-type scanning electron microscope (FE-SEM; Hitachi, S-900) and reflection high-energy electron diffraction (RHEED; JEOL, JEM-200B).

3. Results and discussion

The obtained films were almost transparent and

pale yellowish in color. However, the transparency of the films decreased and the color of the films changed to deep yellow with an increase of Mg content. The Mg contents of these films almost corresponded to those of the target before sputtering within the accuracy of EPMA analysis.

3.1 Lattice constant and tetragonality

Figures 1 and 2 show, respectively, the lattice constant and tetragonality c/a as functions of the film composition. Both *a*- and *c*-parameters in the region of $x=0-0.0075$ appear almost constant but those of samples with Mg addition are sharply reduced with increasing Mg content, compared to those of the sample ($x=0$) without Mg addition in Fig. 1. This result may be explained by assuming that the added Mg (ionic radius: 0.066 nm) was incorporated into the lattice vacancies of Ti (B site, ionic radius: 0.068 nm) with the approximate ionic radius created by adding La of 10 mol% into PbTiO₃, resulting in an extremely small contraction of *a*- and *c*-parameters. On the other hand, the *a*-parameter gradually increased, while the *c*-parameter and c/a decreased with increasing Mg content in the region of $x=0.010-0.025$, as seen in Figs. 1 and 2. These results may also be explained by the presumption that Mg exceeding 1.0 mol% was introduced into the *a*-axial direction of the crystal structure as interstitial atoms, while additional Mg (0.066 nm) entered the A-site vacancies (Pb: 0.124 nm) created on the

Fig. 1. Lattice constants as a function of the film composition. □ *a*-parameter, ○ *c*-parameter.

Fig. 2. Tetragonality c/a as a function of the film composition.

basis of the relation of charge balance when Mg was substituted into the B-site vacancies, resulting in an increase of *a*-axial length and a decrease of *c*-axial length. Thus, we presume that the change in lattice constants caused by the disappearance of lattice defects upon addition of Mg in the former region is extremely small, but that caused by the creation of other lattice defects in the latter region is substantial. On the basis of this reasoning, the principal Mg-solubility at the turning point in the vicinity of 0.75 mol% is considered to change from substitutional solubility to interstitial solubility.

3.2 *c*-axis orientation

X-ray diffraction patterns of PLM2.5, PLM10, PLM15 films and PLM10 powder for target material are shown in Figs. 3(a), (b), (c) and (d), respectively. Many peaks are appreciably observed in the X-ray diffraction pattern of the PLM10 target powder. This result is in good agreement with a typical pattern of polycrystalline PbTiO₃ with the tetragonal perovskite structure. On the other hand, only (001) and (100) peaks are observed and other peaks disappeared almost completely in the X-ray diffraction patterns of these films, as indicated in Figs. 3(a)–(c). Additionally, it is found that (001) peak positions observed in Figs. 3(a)–(c) shift towards the higher angle considerably more than the (001) one in Fig. 3(d); on the contrary, (100) peak positions observed in Figs. 3(a)–(c) shift slightly more towards the lower angle than the (100) one in Fig. 3(d). These differences between thin films and polycrystalline powder can probably be considered to be due to the large internal strain and stress resulting in the process of fabricating thin films with preferentially (001) orientation. Next, the X-ray intensities of (001) peaks on the obtained films are markedly stronger than those of (100) ones in the same samples, as shown in Figs. 3(a)–(c). These results indicate that all fabricated films are highly *c*-axis orient-

Fig. 3. X-ray diffraction patterns of *c*-axis-oriented PLMT films and PLM10 powder.

(a) PLM2.5 film, (b) PLM10 film, (c) PLM15 film, (d) PLM10 powder.

ed. The degrees of *c*-axis orientation of Figs. 3(a)–(c) derived from Eq. (1) are 0.99, 0.98 and 0.96, respectively.

Figure 4 shows the degree of *c*-axis orientation α as a function of the film composition. α decreases linearly with an increase of Mg content. The rate of decrease is estimated to be 0.012/atom% (Mg) from the slope of a straight line obtained by the method of least squares. This linear decrease of α is presumably due to the substantial increase of Mg-interstitial solubility into the *a*-axial direction of the crystal structure with increasing Mg content. On the other hand, α (=0.94) of PL10 ($y=0$) films was a little lower than those (=0.96–0.99) of samples shown in Figs. 3(a)–(c).

3.3 Crystallinity

Figure 5 shows the half-width $\Delta\theta$ of (001) reflection as a function of the film composition. $\Delta\theta$ of PL10 films as the starting material is 0.72°. $\Delta\theta$ markedly decreased with an increase of Mg content, and eventually, that of PLM7.5 film exhibited a minimum value of around 0.61°. This result indicates that $\Delta\theta$ decreases sharply due to the reduction of the lattice defects (Ti vacancies) with an increase of Mg-substitutional solubility. Thus, the crystallinity of PLM7.5 film was significantly improved in this study. In contrast, $\Delta\theta$ gradually increased with an in-

Fig. 4. The degree of *c*-axis orientation α as a function of the film composition.

Fig. 5. The half-width $\Delta\theta$ of (001) reflection as a function of the film composition.

crease of Mg content after the turning point of composition $x=0.0075$. This result can be explained by assuming that $\Delta\theta$ gradually increases due to the increase in lattice defects (Mg interstitial atoms) newly created by adding Mg above the limited value (around 0.75 mol%) of substitutional solubility into the B-site vacancies, and that the crystallinity lowers. It was found that thin films with compositions in the vicinity of PLM7.5 have particularly good crystallinity on the basis of the previous results.

3.4 RHEED observation

The measurements of c -axis orientation by the method of X-ray diffraction previously described provide accurate information on the direction perpendicular to the film surface. To investigate the three-dimensional growth direction of these films, it is necessary to analyze the surface structure by means of RHEED observations. Typical RHEED patterns of c -axis-oriented PLT and PLMT films are shown in Fig. 6. Figures 6(a), (b) and (c) represent PL10, PLM7.5 and PLM15 films, respectively. From the diffraction patterns of Figs. 6(a) and (c), the spot patterns of (001) plane are apparently observed. These patterns show that PLT and PLMT films were grown on the MgO substrates epitaxially. On the other hand, Fig. 6(b) shows a good symmetrical pattern, the so-called "Kikuchi pattern",¹⁰⁾ in place of the spot pattern. The Kikuchi pattern is, in general, known to appear only in crystal surfaces showing excellent flatness and crystallinity with extremely small amounts of lattice defects. Therefore, these results suggest that the flatness and crystallinity of PLM7.5 film with the least amount of lattice defects are considerably better than those of PL10 and PLM15 films with various lattice defects, such as Ti vacancies and Mg interstitial atoms. Moreover, these RHEED observations correspond to the variation of $\Delta\theta$ with increasing Mg content mentioned above.

3.5 FE-SEM observation

The FE-SEM micrographs of the cross sections of PLM7.5 and PLM10 films are shown in Figs. 7(a) and (b), respectively. From FE-SEM observations, the columnar or fiber texture in films is not observed; thin films with the compositions of PLM5–10, in particular, appear rather dense in the present study.

4. Summary

Highly c -axis-oriented lanthanum- and magnesium-modified PbTiO_3 (PLMT) thin films were successfully prepared on (100)-oriented Pt film electrodes/(100)MgO single-crystal substrate by rf-magnetron sputtering method. The c -axis orientation,

Fig. 6. RHEED patterns of c -axis-oriented PLT and PLMT films. (a) PL10 film, (b) PLM7.5 film, (c) PLM15 film.

Fig. 7. FE-SEM micrographs of the cross sections of PLM7.5 film (a) and PLM10 film (b).

crystallinity, and structure of surface and cross section of films obtained were investigated in details. As a result, thin films with the compositions of $\{(1-x)\text{Pb}_{0.9}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3 + x\text{MgO}\}$, where $x=0.005\text{--}0.010$, show great promise as new element thin-film materials, from the viewpoint of the crystallographic properties.

Acknowledgment This work was supported, in part, by a grant from the Murata Science Foundation.

References

- 1) Y. Matsui, H. Nakano, Y. Higuma, M. Okuyama, T. Nakagawa and Y. Hamakawa, *IEICE Tech. Rept.*, CPM78-46, 1-8 (1978).
- 2) K. Iijima, R. Takayama, Y. Tomita and I. Ueda, *J. Appl. Phys.*, **60**, 2914-19 (1986).
- 3) R. Takayama, Y. Tomita, K. Iijima and I. Ueda, *J. Appl. Phys.*, **61**, 411-15 (1987).
- 4) R. Takayama, Y. Tomita, K. Iijima and I. Ueda, *J. Appl. Phys.*, **63**, 5868-72 (1988).
- 5) M. Kobune, K. Amakawa, H. Nakayama and M. Onoda, *Seramikkusu Ronbunshi*, **98**, 1231-37 (1990).
- 6) M. Kobune, K. Amakawa, H. Nakayama and M. Onoda, *Seramikkusu Ronbunshi*, **99**, 30-35 (1991).
- 7) M. Okuyama and Y. Hamakawa, *Ferroelectrics*, **63**, 243-52 (1985).
- 8) M. Kobune, K. Akamatsu, Y. Sugie, S. Fujii, K. Nishimura and H. Tomimori, *J. Chem. Soc. Japan*, **1994**, 168-71.
- 9) K. Iijima, Y. Tomita, R. Takayama and I. Ueda, *J. Appl. Phys.*, **60**, 361-67 (1986).
- 10) E. Miyazaki, "Fundamentals and Applications of Surface Science", Ed. by The Surface Science of Japan, NTS Inc. (1991) pp. 203-12.